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Editors
Radoje V. Pantovic
Zoran S. Marković

Vrnjacka Banja, Serbia
12-15 June 2017

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XXV International Conference

"ECOLOGICAL TRUTH"

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ASSESSMENT OF THE ENVIRONMENTAL IMPACT OF AN ITALIAN TEXTILE PRODUCT WITH THE LCA METHOD

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ABSTRACT

In recent years the importance of natural capital in the life of all species on our planet is gaining increasing importance. The main implementation approach suggested to obtain environmental accounting, for a policy of sustainable production and consumption is: Life Cycle Thinking with its operational tool: Life Cycle Assessment, able to calculate environmental indicators and to accompany, the companies in a sustainable transition of production and consumption. In the study, the LCA, was applied to a polyester product, with the aim to identify environmental indicators and advise the company on how to made innovation, in an environmentally friendly manner.

Key words: LCA, polyester, textile, environmental impact, environmental indicators.

INTRODUCTION

The production system developed by men is in stark contrast to the protection of the ecosystem as it is based on the exploitation of limited resources. Much work has been done in the direction of sustainable development, with the use of the green economy, and now we are moving towards the concept of circular economy, however more efforts are needed. The green and circular thinking should guide development in SMEs, green circular management models and businesses that must encourage consumers towards more sustainable lifestyles [7]. SMEs need support to optimize its products through an eco-friendly design that will lead to a competitive advantage [7]. The following work applies the LCA to a company in the textile sector. This sector consists mainly of SMEs, and in recent years has suffered a general drop in production. Despite the stagnant markets, the resilience of the sector is still considerable, there are many companies that try to adapt to changing market conditions, being able to control costs, make production more flexible since the answers uncertain markets. The document in question provides information on the textile industry and the industrial processes used (in particular the preparation of fibers, yarn pre-treatment, and finishing). It provides data and information on emissions pollutants from processes and consumption of resources. The analysis of production cycles performed with the LCA method can create indicators to assess the critical points of the cycle, and be able to make improvements and thus innovation. The results of an LCA study can be used for communication and marketing [8]. The company object of our study, it is geographically located in the South Italy. L 'Stretch Apulia produces more than 40 years home textiles, for a domestic market and they exports to about 20 countries worldwide. The textile fibers are various, the main types of yarns used are: cotton, polypropylene, nylon, viscose, polyester colored or flocks. The company chose a product on which to make the LCA: a fabric made from 100% PET with a small amount of polypropylene (PP) coupled to confer some physical-mechanical characteristics.

MATERIAL AND METHODS

ISO has recognized through 14040 series of standards, the validity of the model LCA defined as a tool for "compilation and evaluation throughout the life cycle of the flows in and out, and the potential environmental impacts, of a product system "and recommended that this type of assessment to companies who wish to adopt an Environmental Management System. the ISO 14040 series is completed, with some technical reports which constitute valuable support for the implementation of standards: ISO/TR 14049 which shows examples of inventory analysis according to the ISO 14041, ISO/TR 14047 which contains examples of assessment of impacts, and for the interpretation of results ISO/TR 14048 defines the data format for the presentation of the study results [13][14][15]. So this is an analysis tool relatively young. For the SETAC instead its definition is objective process of evaluation of environmental burdens associated with a product, process or activity by identifying and quantifying energy, materials used and wastes released into the environment, for assess the environmental impact, and thereby realize the opportunities for environmental improvement [10]. The assessment includes the entire life cycle of the product, process or activity, which includes the extraction and processing of raw materials, manufacturing, transportation, distribution, use, re-use, recycling and final disposal. In summary, the assessment of the life cycle is structured as a matrix input output that, on the lines, lists all the factors of impact on the environment (such as air emissions, the raw materials consumed, waste water, waste products, etc.) and, on the columns, listing all phases and sub-phases (extraction and transport of raw materials, production and transport of intermediate products, production, transportation, distribution, use, reuse and disposal of the product/ service analyzed) that make up the cycle life [1]. Each cell of this matrix shows the contribution of individual stages in the formation of a given factor environmental impact. In this way we highlight the "weak points" (stages with greater impact) and the "strong points", from an environmental point of view [2].

According to ISO 14040 and LCA is divided into four iteratively related phases:

1. Goal and scope definition (described in ISO 14041:1998)
2. Inventory analysis (described in ISO 14041:1998)
3. Life cycle impact assessment (described in ISO 14042:2000)
4. Life cycle interpretation (described in ISO 14043:2000)

The work procedure for LCA can be broken down into seven steps:

1. Analysis of the case to identify significant issues: the case material is browsed and analyzed with focus on the final target audience and the purpose of the study.
2. Definition of the goal and scope for the case: this step includes documentation of the definitions of the goal and scope.
3. Inventory: the need of data and documentation is identified. The data is collected, validated and documented.
4. Preparation and calculation of the inventory profile in the case: data is related to the functional unit. System boundaries can be refined.
5. Compilation of the results into the ISO/TS 14048 data documentation format: document the product system and each included unit process. Document the modeling and validation and supply administrative information.
6. Impact assessment: A full impact assessment includes classification, characterization and weighting.
7. Interpretation: Interpret the results with the focus defined in the goal and scope.

Goal and scope definitions

The purpose of this study is to increase knowledge of the environmental impacts associated with a textile product made from 100% PET yarn, with a low percentage of Polyethylene (PP). The product is used to manufacture the outer cover of the mattress. In the data base are not present in many data on the processes in the textile of PET, since the raw material has emerged in recent years, and also, the machinery, and the technology typically used in the processes, has made significant improvements in recent years. From the environmental point of view, process improvement would lead to an error of assessment of environmental loads when used outdated data, for example a report of the German Textile Machinery Manufacturers [20] argues that, there was a 15% improvement energy efficiency in the last 10 years. In this case the company's technology is modern 2008- 2010. Even the international literature relating to the textile sector show often outdated data. With the LCA we will analyze the life cycle of the product from cradle to grave, for obtain environmental indicators, and provide useful recommendations to the decision-making process. The choices between alternatives will lead to environmental improvements with the help of eco-design and innovation for the production of sustainable products with a gain of market competitiveness. The questions answered by the study are : The most significant pollutants in what process do they form? Which activities of the life cycle of the product contribute most to its overall environmental impact? Between two products with a similar function but different raw material, which is more impactful?

Functional unit

It was chosen as a functional unit: 1 kg of fabric 100% polyester (PET or poly-ethylene-phthalate) which is obtained by using a Jacquard frame, with a wire 167 Denier and a density of fabric 15 picks, coupled with polypropylene (PP).Its function is coverage for a used mattress for 10 years and landfill disposal at end of life. The quantity 1 kg, corresponding to the functional unit required by EC legislation in the application of LCA to textile products to obtain the Ecolabel [8]. On the product will conduct a study on the environmental impacts of all stages and particular attention is paid to pollutants such as' carbon dioxide, VOCs, formaldehyde, and water resources. Afterwards we make another step, one comparison will made between the processes, to see which of them is the most impacting one. At the end, we change the raw material and we calculate the environmental impacts and the related indicators, switching from a synthetic material PET to natural material Cotton.

Inventory analysis

This stage involves the creation of a list of all components of the life cycle of the fabric in PET which fall within the limits of a defined system. There are four main steps: assumptions and system boundaries, cut off and allocation; creating a flowchart; collection of data (Input Material Products and secondary products solid waste, air emissions and water); the calculation the emissions amount in relation to the functional unit. The LCI (Life Cycle Inventory) results, provides a detailed list of all the resources, waste and pollutants of the overall system, that is, of all phases of the life cycle of the product.

System boundaries, hypothesis, cut off

The System boundaries are from the cradle to the grave. In general the processes considered for the study are: the production of resin: polymerization; processes for the preparation of the yarn: spinning, twisting, texturing; processes weaving preparation: warping, dyeing; weaving; finishing; Packaging; use; End of life: disposal in landfill. We make a cutoff for data less than 1% to exclude processes and input or output in accordance with the ISO 14040 section 4.2.3.3[13]. The technology is considered modern, (2008 -2013). From the spatial point of view, geographically the production of the fiber and the polyester yarn is carried out in China, the preparation of the yarn for weaving and the steps of dyeing and warping are carried out in Northern Italy and the steps of weaving, finishing, packaging distribution in southern Italy. The distribution and the use is supposed to happen in Europe, and disposal in Italy. Were considered only the packaging of raw materials and the finished product (cardboard, polyethylene film), because the others would not have made a contribution to the final result (threshold below 0.5%) [10]. Energy Mix: for processes located in Europe, the data of the energy mix were derived from the database Ecoinvent, while the Chinese mix data were taken from industry experts in China and from the literature [11][4][21]. Are considered the transport of raw materials and other additives, and semi-finished products used in the process. The transport of raw materials has been considered as the distance between the store provider or place of production and the company. The means of transport are truck and ship. For the distribution is considered an average distance in Europe. For disposal an average distance of 400 m^2 from the house of the consumer at the point of land filling. The phase of use in this case is to low impact because there are no maintenance, and is not expected use of water or chemicals for washing. The period of use of 10 years is obtained from an average life of the mattresses, the data obtained by the experts of the sector [6]. For the allocation, there are no secondary output products and the process has one only function. There is only a part of tissue discarded at the end of the weaving stage , this is called swarf, and is recycled totally.

Flowchart PET Fabric production

The flowchart in Fig. N. 1 describes all stages of production of PET fabric product, from cradle to grave. The flow chart Fig. N. 2 shows in detail the processes that occur in China: the production of polyester fibers, and processes for producing the PET yarn.

Data sources

The data are hierarchically divided into three categories. The first are of the direct data collected in companies and by industry experts, the second from the data collected by existing international literature and finally a when there is no data to process itself used the database Ecoinvent 2.0 [5].

PET fabric processes

PET fiber production

The polymers used in artificial fiber PET are formed by a chemical reaction: the polymerization. For the continuous manufacture of polyester fibers, l ' terephathalic acid and ethylene glycol are first passed through the primary and secondary esterifies to form the monomer [18]. the process used require the use of solvents, The IPPC regulations 2003 reports that the value of VOC emissions during the polymerization and production of polyester fibers must not exceed 1.2 g / kg of produced polyester resin. The production of PET requires the use of catalysts such as antimony oxide or antimony acetate. Therefore antimony is present as a residue in the polyester. The content of antimony in polyester fibers commercial shall not exceed 260 ppm [6].

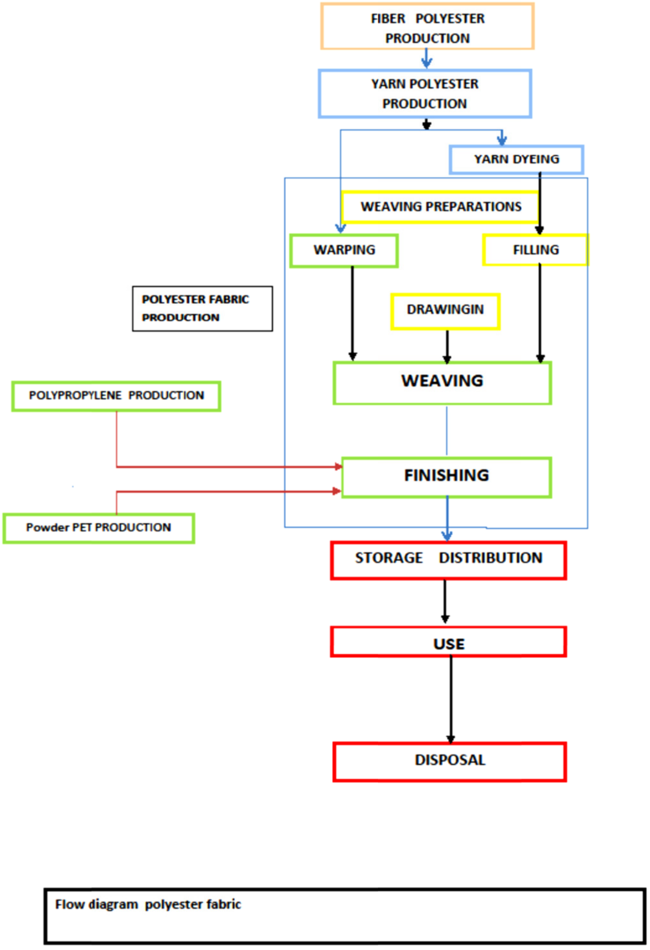

Figure 1. Flowchart of the cradle to the grave of a Polyester fabric product of Apulia Stretch, personal processing.

PET yarn production: Spinning, Twisting and Texturing

The Spinning, refers to the process of formation of the wire from the polymer. The fibers are formed by forcing a fluid or viscous polymer solution through small orifices of a die and immediately solidify or precipitate the resulting filaments. For the polyester, the different processes of melting and spinning commercial are classified according to the degree of molecular orientation in the fiber, this operation increases the crystalline of the fiber, modifying the mechanical properties. VOC emissions associated with the fiber spinning filament appears to be the most significant, with 10.3 g / kg to the value indicated BAT [6]. Twisting process gives a fiber bundle cohesion is necessary to obtain the resistance values required for textile processing. The twist is obtained by rotating a beam of parallel fibers, around its own axis. Texturing is a processing step that is applied to the synthetic yarn, to produce more flexibility, softness, appearance and characteristics similar to the natural ones. This is achieved in many ways, ultimately making with a thermal and mechanical deformation of the individual filaments and varying their spatial arrangement(Fig. N 3).

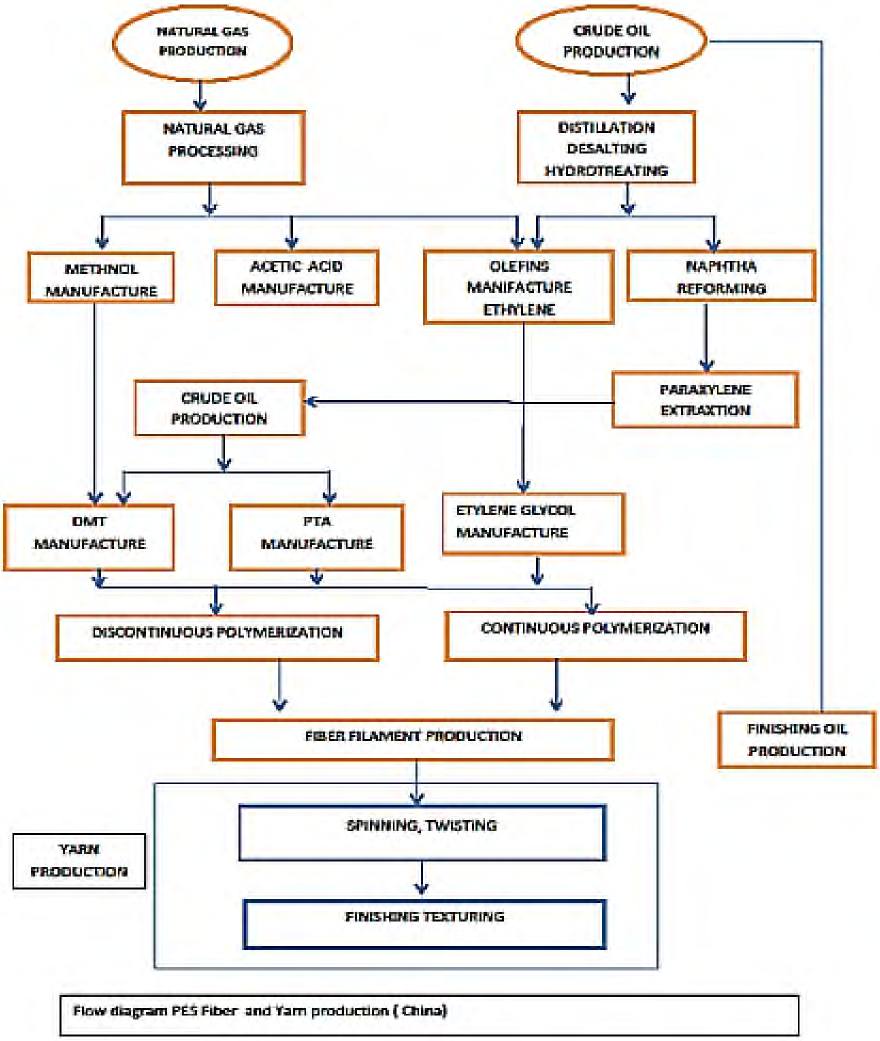

Figure 2. flow diagram of PET fiber production and yarn PET production, personal processing

Warp yarn production: warping

The preparation of the threads for weaving includes two processes. This process is used to prepare the warp yarns. The yarns initially settle on large spools or cones, which are placed on a rack. The warp yarns are then carried out, and pass through a solution of oils, waxes, and other additives used in conjunction with sizing agents to increase the softness and flexibility of the yarn. These substances form a coating that protects the wire against the barb or l 'abrasion during weaving [9].

Weft, yarn dyed: deyng

There are several types you process used to fix the color on the yarns. the process considered in the case study is the Thermosol. the dyeing process shown a series of wash tubs in which you use a lot of water. the ratio is about 1: 100 by volume with the yarn. The dyeing operation is among the stages that a higher environmental impact of the chain due to the large amount of water and energy and chemicals used. [17][19].

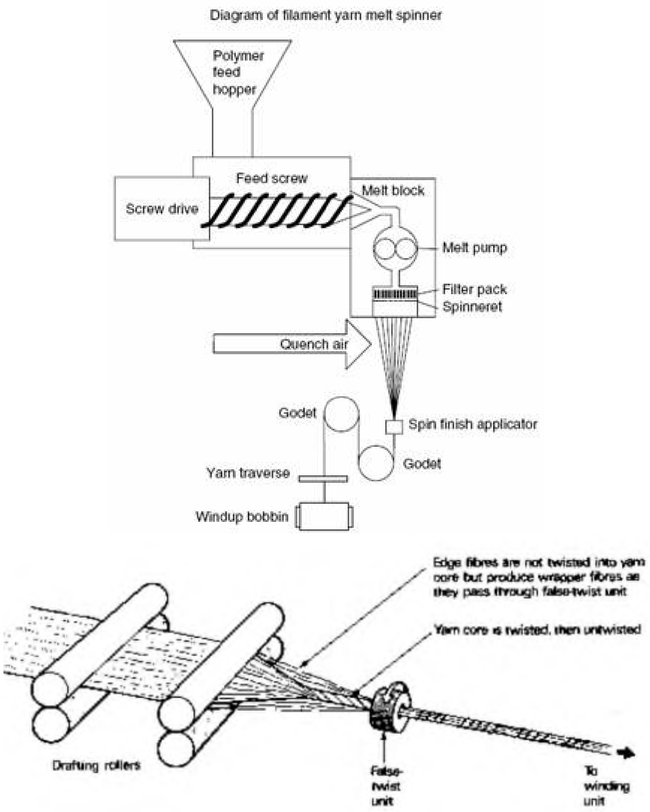

Figure 3. Yarn manufacturing PET, and twisting source, source EPA 1996.
PET fabric production: weaving

The Fig. N. 4, show the frame used for the analyzed product of 'Apulia Stretch in working phase. The frame requires a high amount of electrical energy, this is one of the critical point of the process. Technical consumption of a frame is about 9 Kw/h for the tape loom, and 19 Kw/h for air loom.

Figure 4. Looms APULIA Stretch

PET fabric finished: finishing

In the case of the product analyzed, the finishing stage is called laminating. The fabric coming out from the frame wrapped on a tube, is placed under the laminating machine, and passes on a rotating drum kept at a high temperature together with a non-woven polypropylene (PP). As binder we using a powder in PET. With the heat around (120 degrees) and the slight pressure the various parts are joined in a single fabric that is rewound on another tube. This process requires a large amount of electricity(Fig. N. 5)

PET fabric: storage, use

The fabric is located on a large roll and must be prepared for sale in the measures of linear meters, required by the customer. A little machine: cuts, creates rolls and packages the fabric. The machine through the heat heat-seals the roll with a polyethylene film. It needs electricity, about 6 Kw/h. For use process, we considering the average length of a mattress 10 years. This stage is a low environmental impact, since maintenance is not carried out, the product is not washed so not on water or chemicals.

Figure 5. Finishing machine, Apulia Stretch

PET fabric disposed

It is considered disposal, 100% of polyester fabric in the landfill. For transport, we set an average distance of 400 km from the consumer to the landfill. The process data are taken from the database Ecoinvent [5].

Impact Assessment (LCIA)

After you have completed the LCI, the next step is the evaluation of the impacts of the life cycle (LCIA). To do this you use the methods of assessment, in this study the LCI data are processed with two method: ReCiPe, and Ecological Footprint.

RESULTS AND DISCUSSION

From evaluation of the LCI inventory, you obtain a series pollutants flows. From the list of elementary streams we extrapolate the quantitative data obtained for some substances considered most significant by the standards of the textile industry, and water consumption is calculated as a resource, because the latter has a strategic importance to the latest directives of the European community. In the following graph Fig. N. 6, it is shown the concentrations of carbon dioxide (CO2), formaldehyde and volatile organic compounds(VOC) and the liters of water used. These substances are: quantified for each process in the life cycle of the product.

It is observed that: the amount of water used is much greater in the process of dyeing yarn PET, corresponds to 69.6% of the total water used in the entire system of product analyzed. In addition, there is 14.2% for the production phase of the fiber and the yarn and the 10. 6% for the weaving stage. The process that produces the largest amount of CO2 is the production of the fiber and yarn PET that in our study have been associated together, as they are made by the same Chinese company, it has 60.5% of the total. Subsequently, there is the weaving process with 13.5% and that of the warping with 12% [3][4]. Formaldehyde is known to be a typical emission of the processes of dyeing and finishing, as confirmed by the results. They are 58.8% of the total resulting from the dyeing phase, and 40.1% of the finishing [6].The volatile organic compounds (VOC) are more present in the production phase of the fiber and yarn PET accounting for 90.1%.

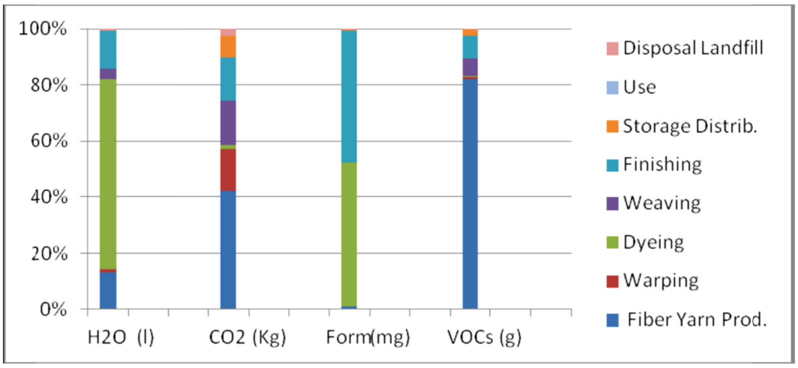

Figure 6. Inventory results, elementary flows: water, CO2, Formaldehyde, VOC

With the Recipe method we calculate the environmental impacts and by aggregating, we get the environmental damage indicators. Please remember that they are three: Damage to human health, Damage to ecosystems, Damage to the availability of resources, end total.

The graph Fig. N. 7 shows the results. The production of fiber and yarn PET step is the most impactful, considering the damage on the human health, on the quality of the ecosystem and the use of resources. Its contribution on the overall impact of the product system is 74.4%. Subsequently, the critical phases is disposing of fiber PET in landfills. It accounts for 7.1% of it. At follow, the phase of yarn dyeing PET with 7%, finishing 6.7%, the preparation of warp for weaving 2.6%, then, the weaving jacquard looms with 1.4% and finally the packaging and distribution with 0.8%. The use phase of the product could also be eliminated from the study because it is insignificant, as its percentage is zero.

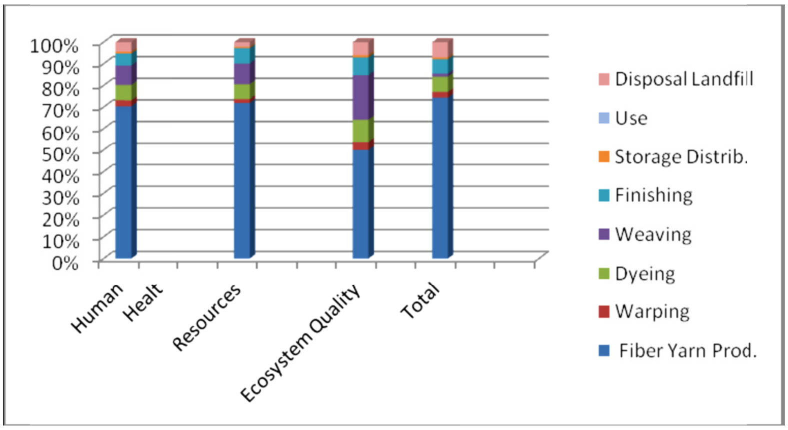

Figure 7. Comparison of environmental damage indicators ReCiPe for each process

Comparison between two row material: cotton end PET

In this phase of the study two products were compared obtained with two different materials: cotton (CO) a natural fiber and polyester (PET), a synthetic fiber. The methods used for the impact assessment are the ReCiPe and the Ecological Footprint. The graphs in Fig. N.8 show the comparison between the environmental indicators of the product Cotton and the product PET, considering all the midpoint indicators of the ReCiPe method. It is possible to notice at first glance that the product in cotton is generally more impactful.

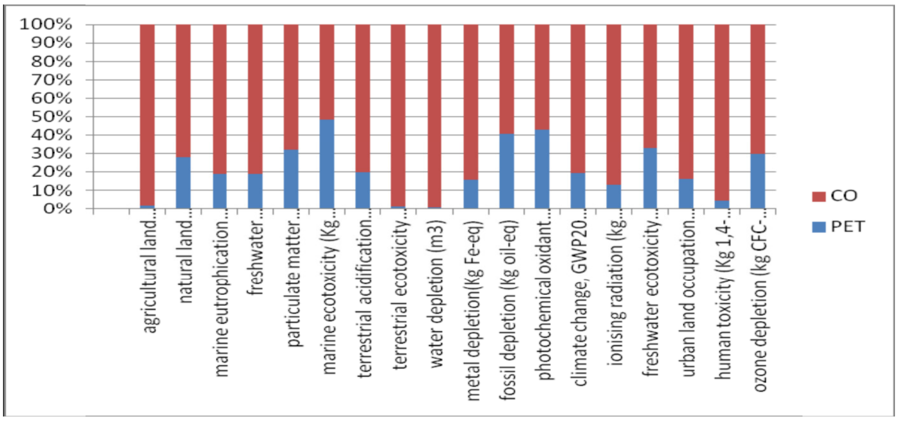

Figure 8. Impact result PET Fiber and Cotton Fiber, Method ReCiPe midpoint

In the following graph, the results obtained with the ReCiPe method aggregating indicators, are shown: human health, resource consumption, and quality of the ecosystem and their total value. As you can see from the graphs, the cotton fabric has higher values in eco points for the quality of the ecosystem and human health, while for the use of the resources Polyester has a higher score, due to the use of natural gas and in the oil phase polymerization and fiber production. The total of the indicators, shows that polyester fabric is however less impactful than cotton, because the second one requires a series of chemical products for the cultivation of the natural resource and for the treatments of the crude fiber (Fig. N. 9) and (Fig. N. 10) [16].

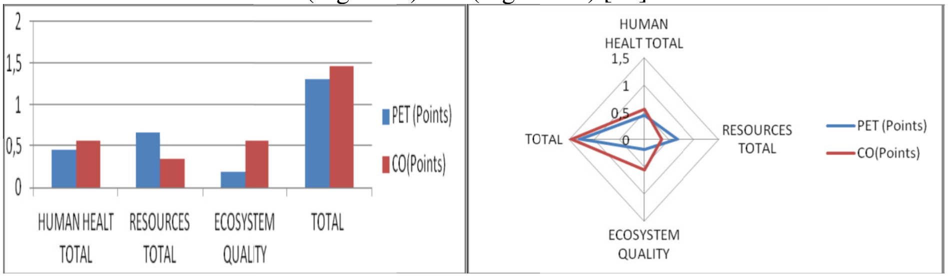

Figure 9 and 10. Comparison PET fabric and Cotton Fabric, ReCiPe endpoint indicators

With the Ecological Footprint method, we calculate the indicators clearly showing land consumption in square meters of land. The product based on cotton has a high impact clearly due to the extended used for cultivation, while square meters of land relative to CO2 are almost similar. Considering the total also in this case the polyester fabric is less impactful. Fig. N. 11.

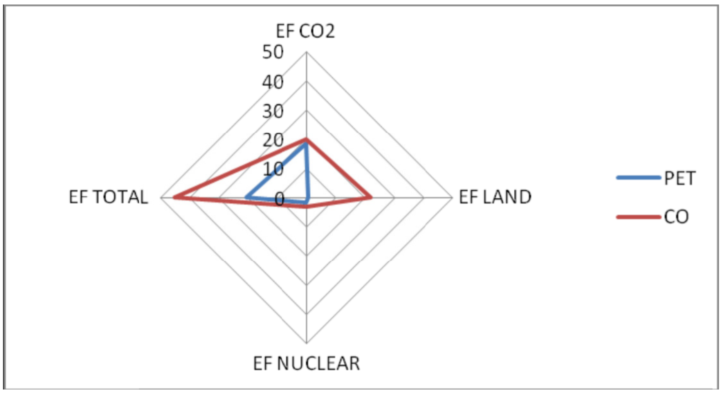

Figure 11. Ecological footprint indicators: comparing PET Fabric to Cotton Fabric.

A summary of the results leads us to the following considerations: the water resource is used more in the dyeing process, we they can recommend to buy, a dope dyed yarn made from a polymer that is colored in the extrusion phase and formation of the yarn to reduce the use of water.

With regard to the CO2, the process that produces the largest amount is the production of the fiber and yarn PET. It is important to remember that this takes place in China. They may advise you to buy the yarn from a country that use energy mix, less polluting.

As for the formaldehyde, dyeing and finishing processes are to be kept under control and for VOC production, the phase of fiber and yarn are important. This means that if in the future the company will certify its product with an Ecolabel [8] it will need to give more attention to these phases.

Finally, if you vary the raw material, comparing Cotton to PET, the latter is less impactful. This is due to the need of soil and water and chemicals for the cultivation of the natural resource and for the treatment of raw fiber. So even if the polyester is obtained from non-renewable resources from these results and from data obtained in the fiber production worldwide is convenient to continue to use this raw material.

CONCLUSION

In general it is recommend that the industry abandon the strategy based only on resource consumption and embrace that of resource saving and innovation. As for the company case study: it is recommended to change the technology of the dyeing yarn where possible, as the consumption of water resources could then be drastically reduced.

Another critical point is the production of fiber and polyester yarn. The contribution of these processes on the total impact is 74.4%. IT is not convenient to change fiber because the cotton is even more impactful than polyester. What we generally recommend is to try to recycle the product. This would alleviate the use of virgin material avoiding impacts occurring during the production of fiber and yarn PET. Recycling activities are present on the Italian territory, but they are more developed for clothing. For home textiles and in this specific case, are not very used. Government policies should encourage recycling in this area. Another option is to use polyester from recycled PET bottles, but that requires improvements for what concerns the mechanical and physical aspect. In the future, fit is possible encourage studies on alternative raw materials, such as waste products of corn processing or the fibers obtained from molasses (waste of sugar production).

REFERENCES

1. Azapagic, A., Perdan, S., 2000.Indicators of sustainable development for industry: a general framework. IChemE Trans. B 2000;78(B4):243–61.
2. Azapagic, A. Perdan, S. 2005. An integrated sustainability decision-support framework Part II: Problem analysis. International Journal of Sustainable Development & World Ecology ;12:112–31
3. Chang, A.,Pashikanti,K., Liu, Y.A., 2012. Refinery Enginnering, Wiley-VCH Verlag Gmbh, Weinheim.
4. Cui ,X,. J. Hong, Gao, M., 2012. Environmental impact assessment of three coal-based electricity generation scenarios in China, Energy 45 952-959
5. Ecoinvent, 2010. Database Ecoinvent version v2.2. The Swiss Centre for Life Cycle Inventories.
6. European Commission(2003) Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for the Textiles Industry July 2003
7. European Commission, 2010. JRC Scientific and Technical Reports, Environmental Improvement Potential of Textiles (IMPRO□Textiles).
8. European Ecolabel, 2012.Revision of the European Ecolabel and Green Public Procurement (GPP) Criteria for Textile Products, for the 2nd AHWG Meeting.
9. EPA,1997.Profile of the textile industry (EPA/310-R-97-009), Environmental Protection Agency, Washington, DC.
10. Guinée J. B., 2002, Handbook on Life Cycle Assessment, Operational Guide to the ISO Standards , CML Leiden University.
11. Hasanbeigi, A., Hasanabadi, A., Abdorrazaghi, M.,2012. Comparison analysis of energy intensity for five major sub-sectors of the Textile Industry in Iran, Journal of Cleaner Production 23 (2012) 186e194.
12. International Organization for Standardization, 2000. ISO/TR 14049 . Environmental management – Life cycle impact assessment – Examples of application of ISO 14041 to goal and scope definition and inventory analysis.

13. International Organization for Standardization, 2003. ISO/TR 14047 . Environmental management – Life cycle impact assessment – Examples of application of ISO 14042.
14. International Organization for Standardization, 2002. ISO/TR 14048. Environmental management – Life cycle impact assessment
15. International Organization for Standardization, 2000. ISO/TR 14049 . Environmental management – Life cycle impact assessment – Examples of application of ISO 14041 to goal and scope definition and inventory analysis.
16. L'Abbate P. , De Koning A., Dassisti M., 2014. Comparative LCA of the products of the textile chain. Case study Apulia Stretch, ECOMONDO Eco-innovation ,Tools for evaluating the sustainability of products / processes: CTS Ecomondo, Italian Network LCA, ENEA.
17. Nieminen-Kalliala E. , 2003. Environmental indicators of textile products for ISO (Type III) environmental product declaration. AUTEX 209 Research Journal;4, ttp://www.autexrj.org/No4-2003.htm. (accessed 28 April 2012)
18. Mathieu, S,2002. Life Cycle Assessment und o¨kologische Recyclingkonzepte fu¨ r ein Textil aus Polyester (PES). Diplomarbeit, ETH.
19. Nieminen, E., Linke M., Tobler M. & Vander, Beke, B., 2006, EU COST Action 628: life cycle assessment (LCA) of textile producits, eco-efficiency and definition of best available technology (BAT)of textile processing,journal of Cleaner Production, vol. 15, pp.1259-1270.
20. VDMA, 2009. Blue competence brochure, Conserving resources—securing savings-potential. The comparison, measuring and labeling of energy-efficient textile machinery. VDMA, Frankfurt am Mein
21. Wang, X., Y. Chen, P. Sui, W. Gao, F. Qin, X. Wu, J. Xiong 2013. Efficiency and sustainability analysis of biogas and electricity production from a large-scale biogas project in China: an energy evaluation based on LCA Journal of Cleaner Production 1 -12.

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INDUSTRIAL COMBUSTION AS A SOURCE OF AIR POLLUTION

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ABSTRACT

Combustion is the basis of industrial development for the past 200 years. Combustion systems are used to generate steam and heat in various industrial processes. Nowadays, about 78% of a world energy demands are satisfied by fuels combustion. Unfortunately, combustion is one of the bigger sources of the air pollution. There are various techniques available for pollutants emissions control, such as modification of combustion or post-combustion treatment of flue gasses. For implementation of combustion modification, it is very important to know pollutants formation mechanism and kinetics. The selection of appropriate control technology to minimize emission must be based on environmental, engineering and economic requests. In this paper is concluded that in the modern production and business conditions it is necessary to require technological, economic and ecological criteria in the process of sustainable development.

Key words: combustion, air pollution, industry, fuels, control.

INTRODUCTION

The concept of sustainable development was created as a way of solving the ecological crisis caused by industrial exploitation of environmental resources and the continuous deterioration of its quality, i.e. environmental degradation. Over time, the concept of sustainable development enhanced economic and social dimension. It is essential that the management of the company finds a balance between economic, social and environmental protection elements, in the right way. Complexity of environmental issues, which are primarily the result of accelerated industrial development, is influenced by the comprehension that the traditional economy of these issues can’t solve those problems in an adequate manner. The complexity of sustainable development refers to the integration of different objectives - economic, environmental, social, cultural, physical and other. The link between the economic system and the natural environment is reflected, on the one hand, in the use and depletion of natural resources for production and consumption and, on the other hand, in the creation of waste, as a result of production and consumption realisation, which are transmitted and stored in the environment [1].

The improvement of living standards and rapid industrialization brought up increased energy consumption, not only in developed, but also in developing countries. The largest part of the energy required (88%) is still obtained from burning fossil fuels. According to estimates of the International Energy Agency (IEA), the expected increase in energy consumption goes up to 40% until the year of 2025. Increased fuel consumption leads to increasing emission of pollutants into air.

Reducing of pollutants emission could be achieved by using primary and secondary measures. Primary measures include: pre-treatment of fuels and modification of fuel combustion process. For this modification to be efficient, it is necessary to know the mechanisms and kinetics of the pollutants formation, to impede their evolution. As a secondary measure we can point out pollutants removing from the flue gas by various secondary-post-combustion techniques.

INDUSTRIAL COMBUSTION

Combustion is the rapid reaction of fuel and oxidizer, accompanied by the release of chemical energy with the appearance of the light effects. Chemical energy of fuel is converted into heat, and further optionally, into mechanical work or electricity by combustion of fuels in power plants, industrial furnaces, steam boilers, gas turbines, etc.

Combustion of gaseous fuel is the least harmful to the environment comparing to liquid and solid fuels. The natural gas has the simplest composition, and consists of methane, somewhat others alkanes and minor quantity of CO_2, N_2 and H_2S. The large content of N_2 could be found in manufactured gaseous fuels. Combustion of gaseous fuels can be easily regulated [2].

Liquid fuels are, usually, complex mixtures of a large number of hydrocarbons.The composition of liquid fuel is derived from data of the ultimate analysis expressed as a mass fraction of carbon, hydrogen, sulfur, oxygen, nitrogen and ash [3]. Content of fuel-nitrogen is usually about 2%whereas fuel-sulfur content is around 5% depending on sort of liquid fuel. The pollutant emissions depend strongly on the residue behavior during combustion of fuels.

For the solid fuels characterization, data can be obtained by the ultimate and by the proximate analysis. Proximate analysis gives data on: surface moisture (SM), the inherent moisture in the coal (M), volatile matter (VM), fixed carbon (FC), ash (A) and heating value of coal (HV) [4]. Solid fuels are burned in a variety of systems. Like for example, in large industrial furnaces (boilers for electric power generation) coal is pulverized to a fine powder which is then, introduced into the combustion system. The combustion of fine coal powder has many similarities to the heavy fuel oils combustion. For burning of large particles in smaller systems fixed- or fluidized-bed combustors are generally utilized.

A stoichiometric equation of complete fuel (gaseous or liquid) combustion having the general formulaC_nH_m in air can be written as follows [5]:

$$C_nH_m + \left(n + \frac{m}{4}\right)\left(O_2 + 3.76N_2\right) \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.76\left(n + \frac{m}{4}\right)N_2 \qquad 1$$

where: $\left(n+\frac{m}{4}\right)(O_2)$ is stoichiometric amount of oxygen for complete combustion. For solid fuels, stoichiometric amount of oxygen is determined by the stoichiometric amount of oxygen needed for all combustible fuel components (based on ultimate analysis).

In the case of complete combustion, components present in the combustion exhaust (flue gas) are: CO_2, H_2O and N_2. Due to high combustion temperature, oxidation of nitrogen from air to nitrogen oxides is likely to appear even in the case of complete combustion. During combustion, the formation of certain pollutants is possible: SO_2-fuel-sulfur oxidized, N_2 and NO - fuel-nitrogen oxidized, ash - transformation of noncombustible mineral matter from the fuel.

Combustion is not always complete, so flue gasses can contain unburned or partially burned combustibles. Incomplete combustion occurs when the amount of air supplied is less than the stoichiometric or when there is a poor mixing of fuel and air. Under this condition, the flue gas may contain a mixture of CO, CO_2, H_2, H_2O, NO and unburned fuel (hydrocarbons). For example, if fuel and stoichiometric amount of air are introduced separately into the combustion system, combustion is incomplete owing to the fact that local amount of oxygen is not stoichiometric. In order to achieve complete combustion, the most combustion systems are operated at condition using more than stoichiometric amount of air. Combustion in this case can be illustrated by the equation [5]:

$$C_nH_m + (1+\beta)\left(n+\frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + \beta\left(n+\frac{m}{4}\right)O_2 + (1+\beta)\left(n+\frac{m}{4}\right)3.76N_2 \qquad 2$$

where: β-is excess oxygen and $\alpha = 1+\beta$ - coefficient of excess air.

The combustion conditions are very often defined by equivalence ratio, that is $\phi = 1/\alpha$.

Depending on combustion conditions, α and ϕ may have certain values: $\alpha = 1$and $\phi = 1$for stoichiometric combustion; $\alpha>1$ and $\phi<1$ for combustion with excess air – fuel lean combustion and $\alpha<1$ and $\phi>1$ for combustion with deficient air –fuel rich combustion.

Obviously, a flue gas composition varies on fuel, combustion conditions and combustion system. The maximum release of energy during the fuel combustion is obtained in complete combustion, with minimum excess of air and with exclusive formation of components: CO_2, H_2O, SO_2 and N_2. In practice, combustion processes departure more or less from this ideal case and unburned substances are formed due to: complex fuels structure (such as coals and heavy liquid fuel), imperfections of the combustion system, insufficient oxygen amount. Unburned substances are discharged into the atmosphere with the flue gases, leading to heat energy loss (accompanied by a decrease of the thermal efficiency of the process) and at the same time, causing the air pollution [6]. Therefore, energy efficiency increase of the combustion process is of great importance from both aspects, energy consumption and pollution [7, 8].

COMBUSTION POLLUTANTS AND EFFECTS

Air pollution represents any atmospheric condition where substances exist at concentrations above their normal ambient levels to produce measurable effects on humans, animals, vegetation, or materials [9]. Fuel combustion has numerous byproducts, many of which are pollutants. Nowadays, even CO_2 and H_2O are denoted as pollutants due to their impact on global warming and atmosphere characteristics.

Important classification of air pollutants is according to the way they reach the atmosphere: primary and secondary air pollutants. Primary pollutants are directly emitted to the atmosphere: for example, carbon monoxide emitted from vehicles, sulfur-dioxide and nitrogen oxides emitted from factories and power plants. Secondary pollutants are formed as the result of chemical reactions of primary ones with other constituents from the atmosphere: for example, ozone formed by photochemical reaction of volatile organic compounds and nitrogen oxides. Secondary pollutants are responsible for the smog, eye irritation and material damage.

The most of the air pollutants originate from combustion processes. This includes mobile sources [10] such as automobiles and trucks and stationary sources such as power plants and industrial combustion processes [11].

Sulfur dioxide (SO_2) is formed by the oxidation of sulfur contained in fuel as well as from certain industrial processes that utilize sulfur-containing compounds [12]. SO_2 is a nonexplosive, nonflammable, colorless gas that has irritating odor. High concentrations of sulfur dioxide can cause temporary breathing problems of asthmatic children and adults. Long term exposures to high concentration of sulfur dioxide can result in lung or cardiovascular diseases. The main environmental problems caused by SO_2 are decreased visibility, damage to vegetation and acid deposition (discussed latter).

Nitric oxide (NO) and nitrogen dioxide (NO_2) are two most important nitrogen oxides as air pollutants. They are usually denoted as NOx, while the notation NOy is often used to represent the sum of nitrogen compounds that are products of atmospheric reactions of NOx (nitric acid, nitrous acid, nitrate radical, nitrogen pentoxide and peroxyacetyl nitrate) [13]. Mobile combustion, stationary combustion sources and industrial processes are the largest NOx sources. NO is a colorless gas and a precursor of NO_2 which is an active compound in photochemical reactions that produce smog. NO_2 is a reddish brown gas that gives color to smog and it is more toxic than NO. NOx is a mixture of gases contributing to the heart and lung problems that may be carcinogenic. Nitrogen oxides in the atmosphere are responsible for the formation of: acid rain precursors, nitrate particulates, photochemical smog, ozone in the troposphere and for the global warming.

Carbon monoxide (CO) is a colorless, odorless and tasteless gas, but a highly toxic. The life time in atmosphere is about 2 or 4 months. It is formed during incomplete combustion of fuels. About 56 % of CO emission originates from motor vehicle exhaust. Combustion systems with defined combustion operation controls produce low amounts of CO.

CO is highly poisonous to humans and most animals; it has 200 times higher affinity to hemoglobin than oxygen. CO enters the blood through the lungs and reduces quantity of delivered oxygen to the organs and tissues. Carbon monoxide does not have neither detrimental effect on material surfaces nor produces harmful effects on plant life. In photochemical reactions CO takes a minor role in ozone formation [11].

Particulate matters (PMs) are solid particles or liquid droplets consisting of one or several chemicals. PMs are small enough to remain suspended in air. PMs can be divided according to size into: fine (less than 2.5μm i.e., PM2.5) and coarse particles (less than 10 μm i.e., PM10). Coarse particles appear as a result of materials handling, crushing and grinding operations etc. The chemical composition of PMs can vary widely, depending on their source and they can further react in atmosphere to form other compounds [14].

When PMs enter the respiratory system; larger particles are blocked in the nasal region while smaller particles pass through and deposit in the lungs. In addition, the particulates may be toxic, depending on their chemical composition (adsorption of toxic compounds on particle surface). Furthermore, PMs contribute to smog formation, cause reduction invisibility, can damage materials, but their effects on plants are unknown [9].

Organic compounds are unburned or partially burned fuel from combustion processes or organic vapors from industrial operations. Volatile organic compounds (VOCs) are aliphatic and aromatic hydrocarbons and oxygenated hydrocarbons. Polycyclic aromatic hydrocarbons (PAHs) are generated, to a smaller extent, from combustion processes of fuels while to a larger extent from the incineration of waste (dioxins and furans) and from the chemical industry. Many VOCs are known to be harmful to human health. The concentration of PAHs in ambient air is of concern due to possible carcinogenic effects [14].

Ozone, O_3, is a secondary air pollutant. At the ground level, ozone is formed out of ozone precursors VOCs and nitrogen oxides, and since it represents a major constituent of photochemical smog it is 'bad' ozone. However, ozone in the stratosphere is 'good' ozone and serves to absorb some of the potentially harmful UV radiation from the sun, believed to cause skin cancer.

Smog represents air pollution in large urban regions**.** Two forms of smog are: industrial (London-type) and photochemical (Los Angeles-type) [15].

Industrial smog, known as gray smog, results from the high concentration of sulfur oxides in the air and is generated by the use of sulfur containing fossil fuels, particularly coal.

Industrial smog consists of carbon (soot) particulates, carbon monoxide, and sulfur dioxide which can form sulfuric acid with water vapor. In developed countries, industrial smog is of rare appearance due to pollution controls in industry and energy production.

Photochemical smog occurs in sunny and dry cities with a large number of vehicles. Photochemical smog forms under the influence of sunlight on primary pollutants (NO_x, hydrocarbons, etc.). During these reactions O_3 and oxygenated hydrocarbons are formed.

The variation of daytime pollutants concentration is shown in Fig.1.

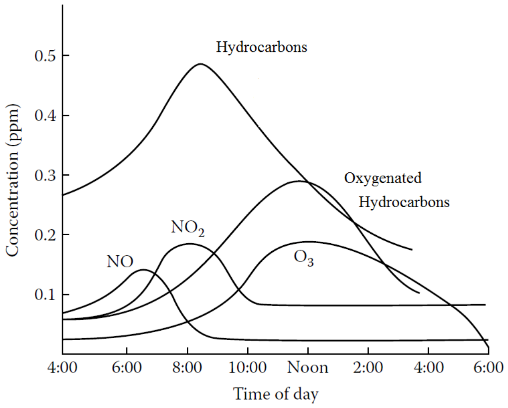

Figure 1. Daytime pollutants concentration (adapted from [15])

Acid rain

In absence of pollution, the typical pH of rain would be approximately 5.6. Acid rain is defined as the rain having a pH less than 5.6. Acid deposition primarily results from the transformation of sulfur dioxide (SO_2) and nitrogen oxides into dry or wet secondary pollutants such as sulfuric acid (H_2SO_4), ammonium nitrate (NH_4NO_3) and nitric acid (HNO_3). Acid rain often represents a regional problem, because a large quantity of SO_2 and NO_2 emitted in one country can be exported to others. Acidic particles and vapors are deposited by wet and dry deposition. Acid rain, fog and vapor spoil the surfaces of plants. Acid rain also depletes supplies of important nutrients (e.g. calcium and magnesium) from soils. Acidification of surface water (lakes, rivers, etc.) induces damage to aquatic ecosystems. Furthermore, acid deposition causes the releasing of harmful elements such as: Al, Pb, Hg and Cd from soils and sediments and is responsible for damaging of materials and structures (e.g. building materials, statues, metals, cars).

Global warming

The Sun radiation is converted to heat at the Earth's surface. To balance this input of solar energy, the Earth emits longer-wavelength radiation, back space. A part of this radiation is trapped and held back by greenhouse gases, resulting in warming of the Earth's surface, known as the greenhouse effect. The main greenhouse gases are: water vapor, carbon dioxide, methane, nitrous oxide, halocarbons and sulfur hexafluoride. Without 'trapping'of radiation by naturally occurring greenhouse gases, the average temperature would be about 30 ºC lower. This Earth's temperature increasing occurs due to the elevated emission of man-made pollutants that cause more of the Sun's energy to be trapped in the atmosphere. There are two major consequences of global warming by the year of 2100: Earth's surface temperature increase by about 3° to 5° C and rising of the sea level.

COMBUSTION POLLUTANTS, FORMATION AND CONTROL

The main categories of pollutants emitted from combustion systems are:
1) products of incomplete combustion (CO, black smoke/soot, organic compounds and particulate matter); 2) pollutants resulting from the inorganic contaminants in the fuel: SO_x, particulates, HCl; 3) NO_x: nitrogen oxides that are the results of reaction of atmosphere or fuel-nitrogen and O_2, and 4) products of complete combustion (CO_2 and H_2O).

SO*x* formation and control

Emission of SO_x is induced by combustion of fuel containing sulfur or in various industrial processes that use raw materials containing sulfur [12]. About 2/3 of emitted SO_x originates from combustion. Sulfur in fuels may be present in organic (thiophene, sulfides, and thiols) or inorganic compounds (pyrite, sulfates) [6]. During the combustion process, the vast majority of sulfur is oxidized to form SO_2, especially under excess air condition (fuel lean). Under deficient air condition (fuel rich), appearance of H_2S and COS is possible. The sulfur trioxide concentration, even under large excess air condition, is only a few percent of sulfur dioxide [16]. SO_x emission reduction can be carried out by: pretreatment (fuel desulfurization), usage of low sulfur containing fuel, combustion modification and post–treatment of flue gas (flue gas desulfurization).

Pretreatment of fuel includes a cleaning process for reducing the sulfur content in coal [15].

Taking into account that almost all of the sulfur in the system will oxidize to SO_x regardless of combustion conditions, very little can be done on SO_x emission reduction by **combustion modification**.The only thing possible is related to sulfur capture inside the combustion system with low operating temperature, namely fluidized–bed combustors,where the bed contains limestone particles.

Flue gas desulfurization (FGD) processes can be classified according to state of scrubber–liquid or a solid into: wet or dry. Also, depending upon whether the resulting end product is disposed of or can be reused, FGD is classified as nonregenerable or regenerable. The major FGD processes are: limestone scrubbing, lime scrubbing, dual alkali processes, lime spray drying and Wellman-Lord process.

NO*x* Formation and control

The primary nitrogen oxide from combustion system is NO, it accounts for more than 95% of the total NO_x. Lifetime of NO in the atmosphere is short (approximately 4 days) because NO readily oxidizes to NO_2.

There are three mechanisms by which nitrogen (from air or from fuel) and oxygen can form NO_x: (1) thermal NO, (2) prompt NO or Fenimore mechanism, and (3) fuel NO. In order to reduce NO_x emission, a detailed knowledge of each mechanism is required.

Thermal NO formation is a function of the combustion temperature and air/fuel ratio. The main reactions of thermal NO, proposed by Zeldovich [13], are:

$$N_2 + O \leftrightarrow NO + N, \qquad 3$$

$$N + O_2 \leftrightarrow NO + O, \qquad 4$$

$N + OH \leftrightarrow NO + H.$ 5

Reaction 5 is important under fuel-rich conditions. Reducing of thermal NO should be achieved by lowering flame temperature, shortening of the residence time in the high temperature region and controlling excess air levels.

Prompt NO is a result of reactions of atmospheric nitrogen with hydrocarbon fragments, it occurs at low temperatures, fuel-rich conditions and short residence times:

$CH\cdot + N_2 \leftrightarrow HCN + N,\cdot$ 6
$HCN + O\cdot \leftrightarrow NH\cdot + CO,$ 7
$NH + OH \leftrightarrow NO\cdot + H.\ \cdot$ 8

Fuel NO may be important during the combustion of fuel that contains significant amount of organically bound nitrogen (e.g., residual fuel oil, coal or waste fuels). Fuel NO is appearing as the result of oxidation of devolatilized nitrogen–containing species (initial stage of combustion) and oxidation of nitrogen from char [13]. Formation of fuel–NO_x is only weakly dependent on temperature, but a strong function of oxygen availability. Therefore, reduction in fuel–NO_x emission cannot be performed by lowering of temperature but by dividing the combustion process into separate fuel–rich and fuel–lean stages.

Dependence of thermal– and fuel–NO_x emissions on equivalence ratio, ϕ, during pulverized coal combustion, is shown in Figure 2.

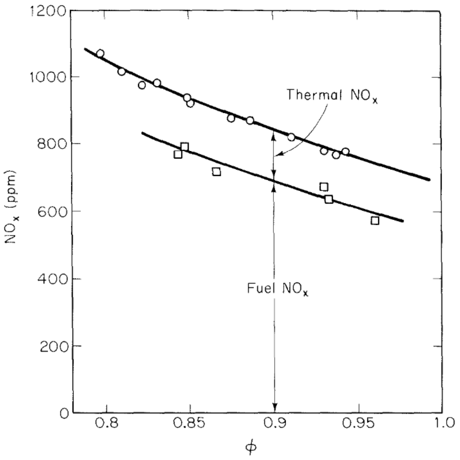

Figure 2. Contributions of thermal and fuel NOx during pulverized coal combustion [17]

The reduction of total NO_x emission can be performed by: combustion modification or by post–combustion treatment of the flue gas. Very often the combination of techniques is used for NO_x emission control.

Combustion modifications reduce NO_x emission by lowering the flame temperature, minimizing residence time or decreasing oxygen availability. The combustion modification and post–combustion treatment are shown in Figure 3.

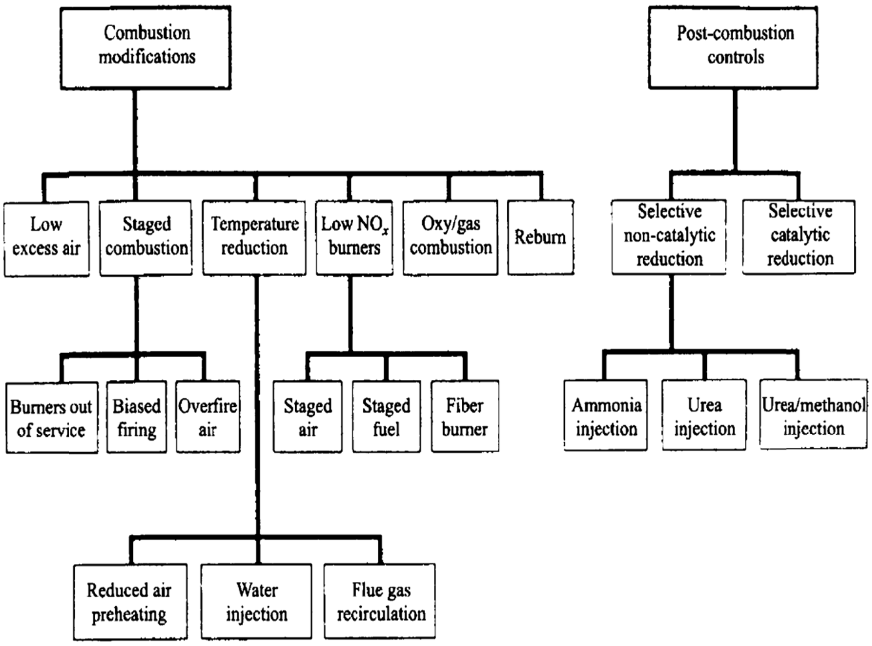

Figure 3. The combustion modification and post–combustion treatment for reducing NOx emission [18]

Lowering of temperature as a measure of NO$_x$ reduction can be done by water–steam injection, flue gas recirculation and reduced preheating air. Low excess air, although easy to perform but with negligible results, reduces NO$_x$ emission by reducing oxygen availability.

Staged combustion as a technique for reduction of NO$_x$ can be done in the furnace or in the burner. Staged combustion in furnace (burners out of service, overfire air) can be performed by air staging (secondary and overfire air) or by fuel staging in the main combustion zone [19]. Low–NO$_x$ burners use the staging air within the burner. In the main combustion zone, combustion takes place under fuel–rich conditions, so NO$_x$ formation is avoided due to oxygen deficiency. The air for the complete combustion is supplied after main combustion zone where the low temperature minimizes additional NO$_x$ formation. Low–NO$_x$ burner is presented in Figure 4.

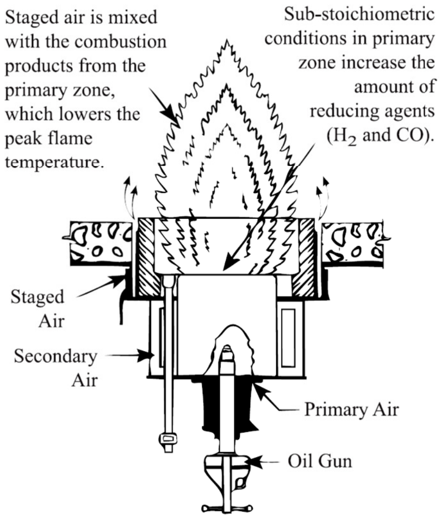

Figure 4. Low-NOx air staging burner[14].

Reburn is a new combination of air and fuel staging, in which additional fuel is inserted after main combustion zone and reduction of NO_x to N_2 is taking place (Figure 5.).

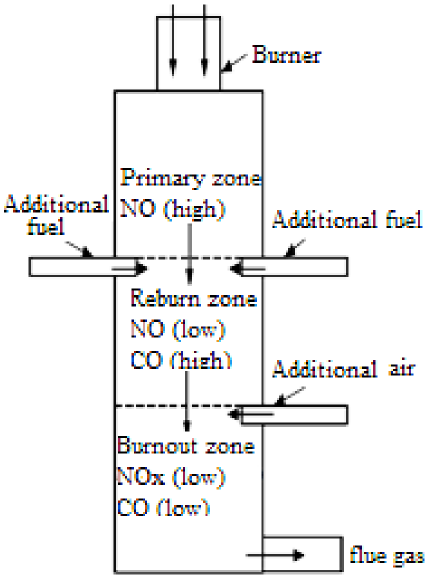

Figure 5. NO_x reduction by reburning [14]

Selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) are widely used for post–combustion reduction of NO_x [20]. In SNCR process, ammonia or urea for reduction of NO_x to $N_{2,}$ are introduced after the main combustion zone within a specific temperature range (1100 – 1200 °C) without the use of catalyst [20]. The rate of reduction of nitrogen oxides is 30 – 50 % for SNCR.

SCR uses a catalyst at around 300 to 400 ^oC. The main advantages of SCR are: low temperature, simple control of process, possibility of using small size catalyst and high efficiency (the rate of reduction of nitrogen oxides is 80 – 95% for SCR).

UNBURNED COMBUSTIBLES FORMATION AND CONTROL

CO

Carbon monoxide is produced in trace quantities in many combustion processes by incomplete combustion. However, the large source of CO is traffic.

Until some combustion modifications for NO_x reduction started to apply, there was generally no concern for CO emission from the industrial processes, there were more than sufficient oxygen, high enough temperature and sufficient residence time for complete CO oxidation. However, due to tendency of reducing air pollution, combustion systems have been modified in such a way that it may be possible to have CO emissions in the flue gas. CO control in industrial combustion systems is completely dependent on the design and operation of the combustion system.

VOC

Like CO, VOCs emission appears due to incomplete combustion, and also as a product of waste incinerators and chemical industry. The composition and quantity of VOCs in flue gases depend on the fuel, on the combustion system and conditions. The range of VOCs that are emitted from combustion systems is too broad. VOCs form in extremely fuel–rich regions of the flame. Control of VOCs in combustion flue gas is normally achieved by adjusting the combustion system to prevent hydrocarbon formation. Removing of VOCs from the flue gas of industrial processes can be applied in two strategies [14]. One is to separate and to recover them using techniques like carbon adsorption or condensation. The other method involves oxidizing the VOCs to CO_2 and H_2O. This process includes techniques like thermal oxidation [21], catalytic oxidation and bio–oxidation.

PARTICULATE FORMATION AND CONTROL

Particulate matter in the most of industrial combustion processes originates from: raw materials, process itself and fuel carryover from combustion system. Particles in the size range 0.1–1 mm are forming by condensation of materials that vaporized during combustion. Particles smaller than 0.1 mm (produced from intermediary products) are formed during combustion while particles greater than 1 mm are the result of the mechanical processes [14]. Incomplete combustion is likely to occur with solid and liquid fuels, but may also appear during combustion of gaseous fuel under fuel–rich condition. Modifying the combustion system means optimization of the combustion conditions in order to minimize the tendency for either forming particulates, or tendency for unburned particulates to leave the system. The main particulate collection systems are: gravity settling chambers, cyclone (centrifugal) separator, wet collectors (scrubbers), fabric filters and electrostatic precipitators [14].

ECONOMICS OF COMBUSTION POLLUTANTS CONTROL

The air pollution control costs are under the influence of various factors such as cost of purchased equipment, the labor costs, costs of capacity, costs of required removal efficiency etc.

Very often, the costs of pollution control systems can be separated into - capital and annualized costs. Direct costs of purchased equipment, the labor and materials in order to install the system are included in the capital, while the indirect costs are related to the design, construction, testing and startup outgoings. Annualized costs cover expenses needed for operating and maintaining of the system and furthermore day-to-day operating costs, taxes, insurance, etc. [21]. Both kinds of expenses, capital and annualized are the subject of many variables of the same type that should be considered while selecting and designing the control system. Variables or factors influencing the control system selection, design and costs are including: first, location and state of pollution source (the new one or existing), process parameters (type, size, capacity, continuous etc.), flue gas properties (temperature, pressure, volume, pollutant concentration(s), moisture content etc.), emission limitations, required system characteristics (type, size, capture/collection system, efficiencies and configurations, construction materials, insulation, utilities, instrumentation), waste disposal/ reclaim/ treatment, operating and maintenance materials.

More rigorous emission limitations and accordingly sophisticated control and increased costs can be determined by the location of the plant, local climate and geography. Sometimes, reconstruction costs for installation can greatly exceed the costs of the new facilities due to space restrictions, out-dated process equipment, etc. Furthermore, in the capture and collection systems materials resistant to corrosion are required due to the presence of acidic components. Particle size and electrical properties of pollutants can significantly increase costs and affect the design. Additionally, waste materials must be handled, stored and disposed of in an acceptable manner. Significant expenses can be involved improving land area, treatment/disposal facilities and in bringing utilities to the disposal site [22]. Table 1. lists characteristics of the most commonly used control techniques.

Table 1. Air pollution control techniques (Adapted from [13-14, 21-22].

Technique	Characteristics
Control of SO_2	
Wet limestone process	High capital cost. Low operating cost mainly because limestone is inexpensive. High efficiency. Low reagent cost reduces high cost of operation and maintenance in very large systems.
Dry sorbent injection process	Compared with wet processes, spray dry sorbent injection process has a lower capital cost but a higher variable operating cost due to expensive sorbent. Moderate efficiency. Easy disposal of dry waste products.
Wellman-Lord process	High capital cost. High operating and maintenance expenses due to complexity of a process. High efficiency. Sulfur in the form of sulfuric acid or elemental sulfur may be recovered and potentially sold or used from the resulting stream.
Control of NO_x	
Staged combustion: Burners out of service Overfire air	No capital cost. Moderately high capital cost.
Flue gas recirculation	Moderately high capital and operating cost.
Low-NO_x burner	30–60% NO_x reduction at relatively moderate high capital and low operating costs.
Fuel reburn	40–70% NOx reduction. It has moderate costs, generally higher than those for low-NOx burners and overfire air.
SCR	High capital and operating cost. High NOx removal.
Particulates	
Electrostatic precipitators	High capital cost, very high removal efficiencies, even for very small particles, low operating costs, except at very high removal efficiencies.
Fabric filters	High capital cost, moderate low operating cost, easy solid-waste-disposal.
Cyclone	Low capital costs, possibility to operate under harsh conditions and low maintenance costs.
Scrubbers	Capital cost of scrubbers is often less than that of comparable fabric filters and ESPs, high maintenance costs.
VOCs	
Carbon adsorption	High operating costs, effective removal of compounds. Moderate capital costs.
Wet scrubbing	Low capital costs. High operating costs. Does not remove all VOCs.
Incineration	System is simple. Effective removal of compounds. Suitable for very high loads. Small area required. High operating and capital costs.

SUMMARY

Although combustion is the basis of industrial development for the past 200 years, it is a very significant source of the air pollution, too. In the combustion system it is necessary to start control of almost all combustion generated pollutants. Almost all the sulfur in fuel will oxidize to SO_x regardless of combustion conditions. All of NO_x control depends on the combustion modifications. CO and hydrocarbon control is completely dependent on the design and operation of the combustion system. In the cases when major emission reductions are required, it is necessary to apply post–combustion treatments. It is very important to select appropriate control technology in order to minimize emission of pollutants. Those methods must to be based on adequate environmental, engineering and economic criteria. Only in that case it is possible to realize long term sustainable development.

REFERENCES

1. Riznić D., Urošević S., Vuković M., Stević Z., Ekonomski aspekti održivog razvoja i uticaj na životnu sredinu, *4 th International Conference on Renewable Electrical Power Sources,* Belgrade, Sava centar, 17.18. October, 2016, pp. 139-148.
2. Gilchrist J., Fuels, furnace and refractories, Pergamon Press, 1977, New York.
3. Mahallawy F., Habik S., Fundamentals and Technology of Combustion, Elsevier, 2002, New York.
4. Speight J., Handbook of Coal Analysis, Wiley Interscience, 2005, New Yersey.
5. Tjapkin-Joksimović S., Procesi sagorevanja, TMF, 1987, Beograd.
6. Gaba A., 2010, Air pollution reduction by using low NOx burners for furnaces and boilers, *Environmental Engineering and Management Journal*, pp.165-170.
7. Najdenov I., Raić K., Kokeza G., 2012, Aspects of energy reduction by autogeneous copper production in the cooper smelting plant Bor, *Energy*, pp. 376-384.
8. Najdenov I., Raić K., Kokeza G., 2011, Economic Insight Into Energents Consumption in Cooper Melting and Refining Plants of Serbia Using the Method of Reduction to Conditional Fuel, *Metalurgia International*, pp. 79-86.
9. Boubel R., Fox D., Turner B., Stern A., Fundamentals of Air Pollutions, Academic Press, 1994, London.
10. Ilić I., Vuković M. Štrbac N., Urošević S., 2014, Applying GIS to Control Transportation Air Pollutants, *Polish Journal of Environmental*, pp. 1849-1860.
11. Biocanin R., Stefanov S., Urošević S., Mekić S., 2012, Modeling of Pollutants in the Air in Terms of Fire on Dumps, Ecological Chemistry and Engineerings-*Chemical Inzynieria Ekologicznas S*, pp. 609-616.
12. Šerbula S., Živković D., Radojević A., Kalinović T., Kalinović J., 2015, Emission of SO_2 and SO_4^{2-} from copper smelter and its influence on the level of total S in soil and moss in Bor, Serbia, and the surroundings, *Hemijska industrija* , pp.51-58.
13. Miller B., Clean Coal Engineering Technology, Elsevier, 2011, Amsterdam.
14. Baukal Jr., Industrial Combustion Pollution and Control, CRC Press, 2003, New York.
15. Perkins H., Air Pollution, McGraw Hill, 1974, Tokyo.
16. Annamalei K, Puri I, Combustion Science and Engineering, CRC Press, 2007, New York.

17. Hayhurst N., Vince L, 1983, The origin and nature of promt NO in flame, *Combustion and Flame*, pp 41-57.
18. Turns S., An Introduction to Combustion, McGraw Hill, 2000, Boston.
19. Nikolić J., Grujić S., 2011, Mere i metode za smanjenje emisije oksida azota iz peći za topljenje stakla, *Tehnika*, pp. 393-398.
20. Nikolić J., Grujić S., 2012, Sekundarni postupci smanjenja emisije oksida azota u procesu topljenja stakla, *Tehnika*, pp. 53-55.
21. Wang L, Pereiara N, Hung Y, Air Pollution Control Engineering, Humana Press, 2004, New Jersey.
22. Neverie R., Price J., Enddahl A., 1978, Capital and Operating Costs of Air Pollution Control Systems, *Journal of the Air Pollution Control Association*, pp. 829-836.

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ELECTROCHEMICAL CHARACTERIZATION OF $La_{0.6}Sr_{0.4}CoO_3$ AND $La_{0.6}Sr_{0.4}CoO_3$ DOPED WITH RuO_2 POWDERS AS THE NEXT GENERATION SUPERCAPACITORS

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ABSTRACT

In this study, $La_{0.6}Sr_{0.4}CoO_3$ (LSC) powder and LSC doped with 20 wt.% RuO_2 were investigated as anode materials for supercapacitor. Spherical submicron particles of $La_{0.6}Sr_{0.4}CoO_3$ have been synthesized by ultrasonic spray pyrolysis. Morphology of LSC powder was examined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy. Both powders were examined by X-ray diffraction, which indicated that substitution of Ru for Sr and Co in the base strongly increased the electrocatalytic activity of the oxide. Electrochemical characterization results have shown improvement in capacitive characteristics of doped LSC showing that this material is good prerequisite for supercapacitor.

Key words: perovskite oxide, supercapacitor, cyclic voltammetry, ultrasonic spray pyrolysis.

INTRODUCTION

Nowadays, the development of high energy supercapacitors has received considerable attention worldwide. Supercapacitors, as a new promising energy storage device, are electrochemical energy storage devices that play an important role in energy storage and delivery. They have many advantages such as faster charging/discharging rate, long idle life cycle, higher power energy density and green environmental protection compared to other chemical energy storage devices [1-4]. The boundary of energy and power density of supercapacitors existing between high power electric capacitors and high energy fuel cells can be determined in the Ragone plot.

However, the previous supercapacitors suffer from low energy density [1, 5, 6]. Hence, in order to meet the development of supercapacitors, their energy density should be substantially enhanced without deteriorating their high power capability and cycle life [7]. Since the active materials in electrodes of supercapacitor determine its electrochemical performance and energy storage capacity a lot, numerous new materials have been widely designed and prepared [8, 9]. It is well-known that the performance of supercapacitors is strongly determined by the properties and structures of electrode materials [10]. Thus, many efforts have been made to design and prepare the electrodes of supercapacitors.

Most popular materials today are particle materials, which have high surface areas for charge storage [11, 12]. Among them, transition metal oxides (TMOs) are considered as ideal electrode materials for supercapacitors as they can provide both a high specific capacitance and a high energy density. A promising candidate for application is strontium substituted lanthanum cobalt oxide $La_{0.6}Sr_{0.4}CoO_3$, a perovskite-type material with a mixed ionic and electronic conductivity (MIEC) at elevated temperatures [13]. Perovskite oxide (ABO_3) displays both good oxygen ion and electron conductivity which could provide some oxygen vacancies to enhance the transfer of oxygen ion. These characteristics make them become excellent cathode materials of solid oxide fuel cell and the potential substitution of bifunctional catalyst compared with precious metal catalyst in Li-air batteries [14]. Perovskites have been paid much attention in past decades because of their stable structure, high-temperature sustainability, catalytic property, and crucial role in solid fuel cells and solar cells [15].

The spray-pyrolysis method was applied for synthesis of the starting powders of the cathode ($La_{0.6}Sr_{0.4}CoO_3$) and anode (a samaria-doped ceria-NiO composite powder). In this study, different microstructures of the cathode were obtained by varying the sintering temperature from 950 to 1200 °C [16].

La-doped $SrTiO_3$ (LST) powders were prepared by ultrasonic spray pyrolysis using an aqueous solution of a metal nitrate [17]. SEM images showed that the as-prepared LST powders had a spherical morphology with a diameter of 1 μm. XRD patterns showed that the crystal phase of the as-prepared powders was amorphous and that the powders crystallized to the perovskite phase by calcination at 900 °C. The sintered LST body had the highest electrical conductivity at a La doping concentration (La_x) of 0.1 under a reducing atmosphere.

The material characterization techniques were implemented to acquire the crystallinity, surface area, and porosity. Consequently, the good electrochemical response was obtained from cyclic voltammetry (CV) studies. The as-prepared samples clearly revealed that the perovskite materials are promising candidate for supercapacitor electrode materials. The aim of this work is synthesis and characterization of submicron particles of $La0_{.6}Sr_{0.4}CoO_3$ prepared by ultrasonic spray pyrolysis in one single step.

EXPERIMENTAL

Material synthesis - preparation of LSC and LSC w / 20 wt. % RuO_2 nanoparticles

Lanthanum nitrate, strontium nitrate, cobalt nitrate were used as precursor for the synthesis of $La_{0.6}Sr_{0.4}CoO_3$ submicron by ultrasonic spray pyrolysis. The temperature and pressure control was adjusted using a thermostat and a vacuum pump. Atomization of the obtained solution after dissolution of precursor took place in an ultrasonic atomizer (Gapusol 9001, RBI/France) with one transducer to create the aerosol. The resonant frequency was selected to be 2.5 MHz. The concentration of nitrogen was flushed from bottle to remove air from the system. Under spray pyrolysis conditions, nitrogen overpassed continuously through the quartz tube (at a flow rate of the 3 l/min). Then atomized droplets were further transported by carrier gas to the vertical furnace, company Thermostar, Aachen. After thermal decomposition of transported aerosol in the furnace, the formed nanopowder of $La_{0.6}Sr_{0.4}CoO_3$ was collected with an electrostatic precipitator.

The precursor solution was investigated in water and alkaline solution. It was concluded that the LSC powder was stable both in aqueous and alkaline solutions. Therefore, the process of preparing $La_{0.6}Sr_{0.4}CoO_3$ powder doped with 20 wt. % RuO_2 was firstly suspending LSC in deionized water in ultrasonic bath for 30 min. Afterwards, 40 µl of 0.1 M KOH was addedto adjust pH value from 8.1 to 10. After in the mixture that was continuously stirred the 661µl of $RuCl_3$ solution was added and pH value was adjusted with 100 µl 0.1 M KOH to 8.5.

Characterization

SEM and EDS analysis of strontium substituted lanthanum cobalt oxide $La_{0.6}Sr_{0.4}CoO_3$, a perovskite-type material were performed using scanning electron microscope VEGA TS 5130MM microscope (Tescan).

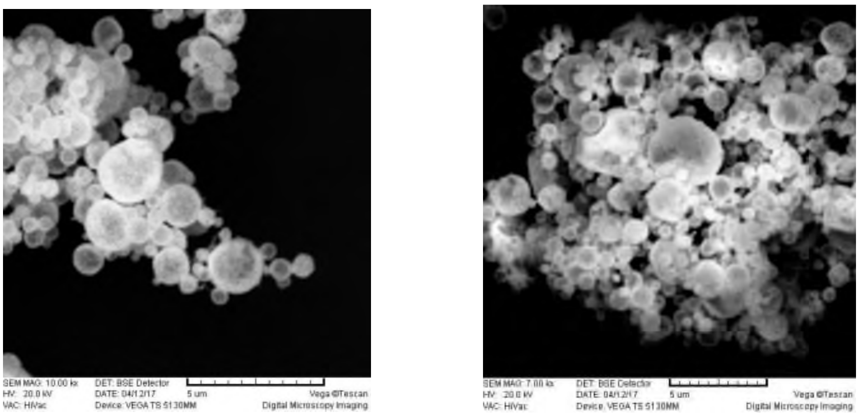
Phase analysis was examined by X-ray diffraction (XRD) measurements on Philips PW 1050 powder diffractometer at room temperature with Ni filtered CuKα radiation (λ = 1.54178 Å) and scintillation detector within 10–82° 2θ range in steps of 0.05°, and scanning time of 5 s per step.

Electrochemical measurements were performed in a three-electrode cell. For this purpose, an electrochemical work station (BioLogic, SP-240) having potentiostat/galvanostat provided with corrosion and physical electrochemistry software and a desktop computer (HP) was used. A platinum foil and Hg/HgO/1M KOH electrode (E° = 0.098 V vs NHE at 25°C) were used as counter and reference electrode, respectively. The working electrode geometric area exposed to electrolyte was 0.39 cm^2. The cell was filled with 0.1 M KOH electrolyte and purged with N_2 for 30 min prior to and continuously during electrochemical measurements.

RESULTS AND DISCUSSION

Scanning electron microscopy

Morphology of the perovskite $La_{0.6}Sr_{0.4}CoO_3$ (LSC) powder was examined by scanning electron-microscopy. SEM photographs of the powder used as supercapacitor before doping with RuO_2 and before dissolution in KOH are shown in Figure 1a, while morphology of the perovskite $La_{0.6}Sr_{0.4}CoO_3$ powder after immersion in 0.1M KOH solution and consequent drying in inert N_2 atmosphere at 150 °C for 3 h is shown on Figure 1b.



a) b)

Figure 1. SEM micrographs of perovskite $La_{0.6}Sr_{0.4}CoO_3$ powder a) before and b) after immersing in 0.1M KOH solution and consequent drying. Magnification a) x10K and b) x7K

As it can be seen, LSC oxide is stable in alkaline solution, with unchanged morphology. Results of SEM micrographs show that material used is in the form fine rounded powder with powder particles ranging from 0.5-4.5 µm. Figure indicates that features of each oxide powder is more or less similar in nature and that it has definite regular structure.

Elemental analysis of the each oxide has been carried out by EDS analysis, and the results, so obtained, are shown in Figures 2 and 3.

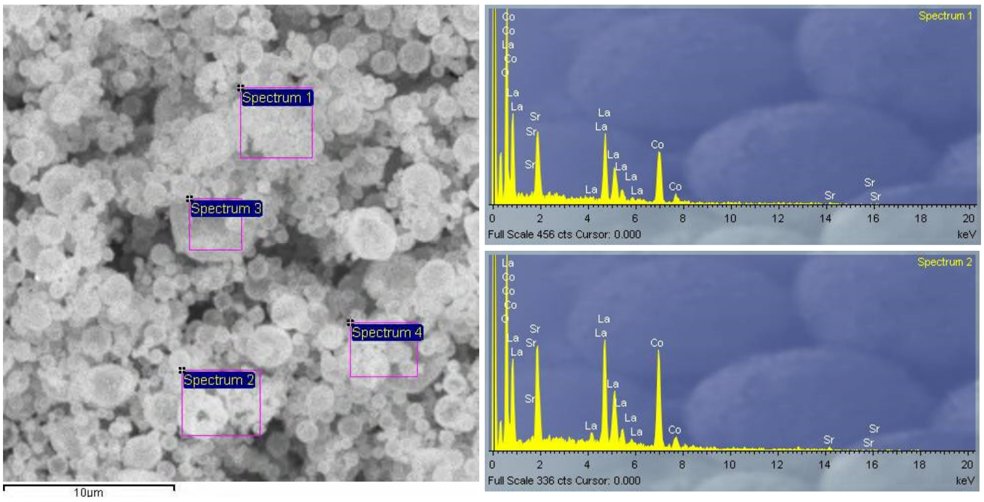


Figure 2. EDS analysis of used LSC oxide with spectrum analysis of site 1 (top) and site 2 (bottom)

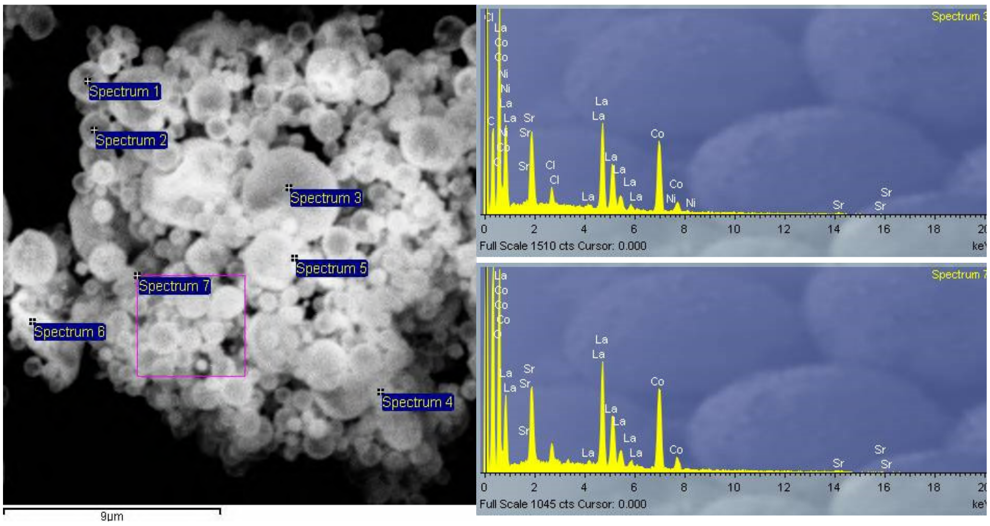


Figure 3. EDS analysis of used LSC oxide after immersion in 0.1 M KOH with spectrum analysis of site 1 (top) and site 7 (bottom)

Table 1 and 2 show atomic % of each element at examined sites. As it can be seen, comparing results from both tables, there is no dissolution of any element in KOH, i.e. the LSC powder is stable in alkaline solution.

Table 1. Elemental analysis of used LSC powder at examined sites

Spectrum	**Co**	**Sr**	**La**	**O**
Spectrum 1	22.73	9.56	14.17	53.54
Spectrum 2	24.17	8.22	14.09	53.52

Table 2. Elemental analysis of LSC powder immersed in KOH at examined sites

Spectrum	**Co**	**Sr**	**La**	**O**
Spectrum 1	23.29	9.42	13.83	53.46
Spectrum 7	23.95	7.89	14.53	53.63

X-ray diffraction analysis

XRD patterns for two powders ultrasonically synthesized e.g. lanthanum strontium cobalt oxide ($La_{0.6}Sr_{0.4}CoO_3$) and LSC doped with 20 wt. % RuO_2 are represented in Figure 3.

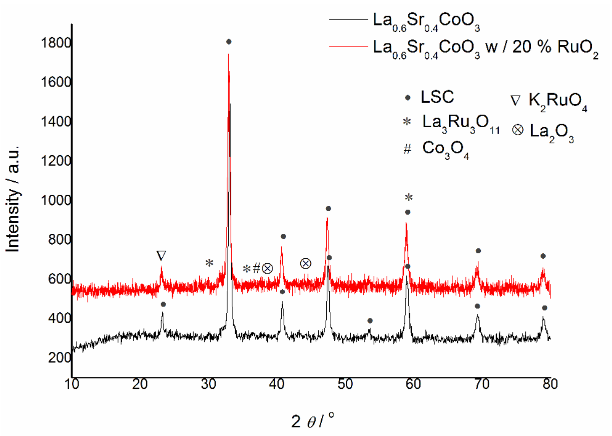


Figure 4. XRD patterns for LSC and doped LSC powders produced by ultrasonic spray pyrolysis

Figure 4 shows the XRD patterns of the as-fabricated sample and powder doped with ruthenium oxide. By comparing the results with XRD pattern (JCPDS PDFNo. 01-89-2528) of the standard $La_{0.6}Sr_{0.4}CoO_3$ sample, it can be seen that all of the XRD peaks of each sample in the 2θ range of 10–80° could be well indexed, as shown in Figure 4. In other words, the LSC powder was of single-phase with rhombohedral crystal structure. For perovskite, as well as other crystalline materials, the variation in the crystal structure may lead to distinct electrocatalytic activities [18]. It was found that LSC has identical rhombohedral lattice which can be indexed according to R-3c space group symmetry (#161). This fact rules out the significant effect that crystal structure may have on the activities [18]. However, new diffraction peaks can be distinguished after doping with 20 wt. % of RuO_2 due to the presence of new Co_3O_4, La_2O_3, $La_3Ru_3O_{11}$ and K_2RuO_4 phases, indicating that the new nanoparticle (NP) compounds were highly dispersed on the LSC surface.

An unknown weak peak at around 2θ=38° was attributed to lanthanum oxide, La_2O_3, according to the JCPDS PDFNo. 00-40-1279 XRD database, which was considered to be the result of a partial decomposition of the LSC [19]. In addition, the diffraction signals assignable to the $La_3Ru_3O_{11}$ and K_2RuO_4 (JCPDS PDF No.01-070-1086 and 01-051-1751, respectively) phase became apparently detected in doped samples, indicating the formation of small amount of ruthenium compound with lanthanum and potassium. Figure 4 also shows the typical XRD peak of the obtained Co_3O_4 in which all the diffraction could be indexed as the cubic Co_3O_4 spinel phase (JCPDS PDF No. 01-078-1969) [20].

Electrochemical analysis

The cyclic voltammograms of LSC and LSC doped with RuO_2 on glassy carbon (GC) substrate were recorded at the scan rate of 20 mV s^{-1} in the potential region -0.2-0.5

V in 0.1 M KOH, at room temperature. A representative curves for each sample are shown in Figure 5. Upon exposure of the GC electrode with LSC and LSC doped with 20 wt. % RuO_2 to potentiodynamic changes, a stable capacitive CV response was registered, in a potential window as wide as 0.7 V in the case of LSC with 20 wt. % RuO_2.

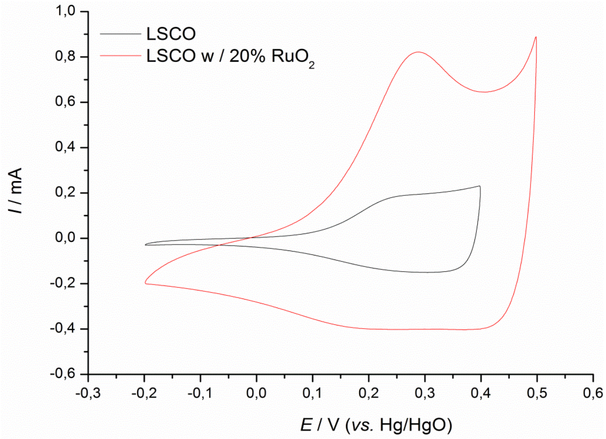


Figure 5. Cyclic voltammograms at a scan rate of 20 mV/s for LSC and LSC doped with RuO_2 at room temperature

The shape of the CV curve of the LSC powder is different with respect to that registered for the LSC powder doped with 20 wt. % of RuO_2. One well-separated peak for the LSC with 20 wt. % of RuO_2 coating at around 0.29 V is seen. The Figure 5 showed that voltammograms of the oxide electrode exhibited a pair of redox peaks, one anodic (E_{Pa} = 290mV) and a corresponding broad cathodic peak (E_{Pc} = 150mV), prior to the onset of oxygen evolution reaction.

The capacitance of LSC was considerably lower, which indicates poor conductivity in the cathodic direction. An LSC powder doped with 20 wt. % of RuO_2 exhibits a considerable increase in the voltammetric capacitance, due to pronounced ruthenium injection into crystal structure of LSC.

CONCLUSION

Capacitive properties of LSC colloidal dispersion and the effects of doping LSC with ruthenium oxide were investigated. SEM-EDS analyses show that LSC material is in the form of fine rounded powder stable in both aqueous and alkaline solutions. The X-ray diffraction study indicated the formation of pure perovskite phase of the material with rhombohedral crystal geometry. The substitution of Ru for Sr and Co in the base strongly increased the electrocatalytic activity of the oxide and the value being highest with 20 wt. % ruthenium oxide. CV studies of the Ru doped LSC material indicate improvement in capacitive response of the material, exhibiting that this material is good prerequisite for supercapacitor. The activity of this oxide is several times higher than the one observed by LSC.

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REFERENCES

1. Cao, Y.; Lin, B.; Sun, Y.; Yang, H.; Zhang, X., Sr-doped Lanthanum Nickelate Nanofibers for High Energy Density Supercapacitors. *Electrochimica Acta*, 174, 41-50, 2015.
2. Arjun, N.; Pan, G.-T.; Yang, T. C. K., The exploration of Lanthanum based perovskites and their complementary electrolytes for the supercapacitor applications. *Results in Physics*, 7, 920-926, 2017.
3. Pan, H.; Li, J.; Feng, Y., Carbon Nanotubes for Supercapacitor. *Nanoscale Research Letters*, 5, (3), 654, 2010.
4. Yang, Y.; Zhang, H.; Zhu, G.; Lee, S.; Lin, Z.-H.; Wang, Z. L., Flexible Hybrid Energy Cell for Simultaneously Harvesting Thermal, Mechanical, and Solar Energies. *ACS Nano*, 7, (1), 785-790, 2013.
5. Yuan, C.; Yang, L.; Hou, L.; Shen, L.; Zhang, X.; Lou, X. W., Growth of ultrathin mesoporous Co3O4 nanosheet arrays on Ni foam for high-performance electrochemical capacitors. *Energy & Environmental Science*, 5, (7), 7883-7887, 2012.
6. Snook, G. A.; Kao, P.; Best, A. S., Conducting-polymer-based supercapacitor devices and electrodes. *Journal of Power Sources*, 196, (1), 1-12, 2011.
7. Wang, F.; Xiao, S.; Hou, Y.; Hu, C.; Liu, L.; Wu, Y., Electrode materials for aqueous asymmetric supercapacitors. *RSC Advances*, 3, (32), 13059-13084, 2013.
8. Wang, G.; Xu, H.; Lu, L.; Zhao, H., One-step synthesis of mesoporous MnO2/carbon sphere composites for asymmetric electrochemical capacitors. *Journal of Materials Chemistry A*, 3, (3), 1127-1132, 2015.
9. Zhang, D.; Yan, H.; Lu, Y.; Qiu, K.; Wang, C.; Zhang, Y.; Liu, X.; Luo, J.; Luo, Y., NiCo2O4 nanostructure materials: morphology control and electrochemical energy storage. *Dalton Transactions*, 43, (42), 15887-15897, 2014.
10. Luo, L.; Liu, T.; Zhang, S.; Ke, B.; Yu, L.; Hussain, S.; Lin, L., Hierarchical Co3O4@ZnWO4 core/shell nanostructures on nickel foam: Synthesis and electrochemical performance for supercapacitors. *Ceramics International*, 43, (6), 5095-5101, 2017.
11. Abdur, R.; Kim, K.; Kim, J.-H.; Lee, J., Electrochemical behavior of manganese oxides on flexible substrates for thin film supercapacitors. *Electrochimica Acta*, 153, 184-189, 2015.
12. Kazemi, S. H.; Asghari, A.; kiani, M. A., High Performance Supercapacitors Based on the Electrodeposited Co3O4 Nanoflakes on Electro-etched Carbon Fibers. *Electrochimica Acta*, 138, 9-14, 2014.

13. Hayd, J.; Dieterle, L.; Guntow, U.; Gerthsen, D.; Ivers-Tiffée, E., Nanoscaled La0.6Sr0.4CoO3−δ as intermediate temperature solid oxide fuel cell cathode: Microstructure and electrochemical performance. *Journal of Power Sources*, 196, (17), 7263-7270, 2011.
14. Sun, N.; Liu, H.; Yu, Z.; Zheng, Z.; Shao, C., The La0.6Sr0.4CoO3 perovskite catalyst for Li-O2 battery. *Solid State Ionics*, 268, Part A, 125-130, 2014.
15. Zhu, J.; Li, H.; Zhong, L.; Xiao, P.; Xu, X.; Yang, X.; Zhao, Z.; Li, J., Perovskite Oxides: Preparation, Characterizations, and Applications in Heterogeneous Catalysis. *ACS Catalysis*, 4, (9), 2917-2940, 2014.
16. Maric, R.; Ohara, S.; Fukui, T.; Yoshida, H.; Nishimura, M.; Inagaki, T.; Miura, K., Solid Oxide Fuel Cells with Doped Lanthanum Gallate Electrolyte and LaSrCoO3 Cathode, and Ni-Samaria-Doped Ceria Cermet Anode. *Journal of The Electrochemical Society*, 146, (6), 2006-2010, 1999.
17. Genji, K.; Myoujin, K.; Kodera, T.; Ogihara, T., Synthesis and Electrical Properties of La Doped SrTiO3 Powders by Ultrasonic Spray Pyrolysis. *Key Engineering Materials*, 582, (9), 115-118, 2013.
18. He, J.; Sunarso, J.; Zhu, Y.; Zhong, Y.; Miao, J.; Zhou, W.; Shao, Z., High-performance non-enzymatic perovskite sensor for hydrogen peroxide and glucose electrochemical detection. *Sensors and Actuators B: Chemical*, 244, 482-491, 2017.
19. Park, J.-S.; Chung, W.-H.; Kim, H.-S.; Kim, Y.-B., Rapid fabrication of chemical-solution-deposited La0.6Sr0.4CoO3−δ thin films via flashlight sintering. *Journal of Alloys and Compounds*, 696, 102-108, 2017.
20. Che, H.; Lv, Y.; Liu, A.; Mu, J.; Zhang, X.; Bai, Y., Facile synthesis of three dimensional flower-like Co3O4@MnO2 core-shell microspheres as high-performance electrode materials for supercapacitors. *Ceramics International*, 43, (8), 6054-6062, 2017.

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NONTHERMAL PLASMA IN WATER TREATMENT

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ABSTRACT

Nonthermal plasma is a promising technique in water treatment**.** Reactive oxygen species (ROS) and reactive nitrogen species (RNS) generated in dielectric barrier discharges are determined dependent on the introduced energy density. The efficiency of the water falling film dielectric barrier discharge reactor in treatment of different organic contaminants was examined. The influence of the catalyst, different inorganic salts and concentration of contaminants on reactor efficiency were studied. After treatment the toxicity of treated samples was examined. Based on our results non-thermal plasma can be successfully used in contaminated water treatment.

Key words: water treatment, advanced oxidation process, non-thermal plasma, dielectric barrier discharge.

INTRODUCTION

One of the most important problems of modern society is the problem of water supplying. The quality of water used for drinking water preparation significantly decreases due to water pollution mainly originating from domestic and industrial sources. Conventional water treatment processes, including physicochemical methods (coagulation-flocculation, sedimentation and filtration) and biological treatment, often could not satisfy the desired quality of effluent water due to refractory or toxicity of present compounds.

New technologies based on advanced oxidation processes were developed for treatment of toxic and refractory dissolved organic compounds[1,2]. Advanced oxidation processes (AOP) are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize the majority of complex chemicals present in the effluent water. Hydroxyl radical is the strongest oxidant that can be applied in water, and through a complex cascade of oxidative reactions it can oxidize any organic compound present in the water matrix. It reacts non selectively and organic contaminants are quickly fragmented and converted into small organic molecules. It also removes some heavy metals in the form of precipitated hydroxides in higher oxidation states. During AOPs, the disinfection of water can also be achieved which provides an integrated solution in water treatment. The product of complete reduction of hydroxyl radical is water, so AOPs theoretically do not introduce new hazardous substances into the water. Another advantage of AOPs over classic methods for wastewater treatment is the possibility of doing the treatment at ambient conditions, *i.e.* atmospheric pressure and room temperature. AOPs show great flexibility in practical usage, because of the fact that they can be used separately or in combination with some other classic methods for water treatment. Hydroxyl radicals are produced by one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide). Some of the well described processes for hydroxyl radical formation are: photocatalysis, Fenton reaction (Fe^{2+}/H_2O_2), photo-Fenton reaction ($Fe^{3+}/H_2O_2/h\nu$), UV/H_2O_2, peroxone reaction (O_3/H_2O_2), O_3/UV, ionizing radiation, vacuum UV, and ultrasound. Some of them, like the chemical combinations of H_2O_2, O_3 and UV, Fenton's reagent, electron beam have already been used at full scale in water treatment.

Nonthermal plasma produced in water solutions forms the basis of innovative AOPs for the water treatment[3,4]. Plasma is defined as a neutral ionized gas. It is constituted of particles in permanent interaction; the particles include photons, electrons, positive and negative ions, atoms, free radicals and excited or non-excited molecules. The classification of plasma is based on the relative energetic levels of electrons and heavy species of the plasma. Thermal plasmas are obtained at high pressure (≥105 Pa) and need substantial power (up to 50 MW) to be observed. This type of plasma is found, for example, in plasma torches and in electric arcs. Nonthermal plasmas are obtained at lower pressures and use less power. They are characterized by an electron temperature much higher than that of the gas (macroscopic temperature) and consequently do not present a local thermodynamic equilibrium. Such plasma can be generated by electric discharges in lower pressure gases.

The nonthermal plasma process can remove chemical and biological waste in all three states (gas, liquid and solid). The method can be used in treatment of different contaminants present in wastewater with both high and low concentration of organic matter, even in a large flux. Nonthermal plasma produced by gas discharges in presence of water generates many reactive oxygen and nitrogen species, like ozone, hydrogen peroxide, hydroxyl radical, nitric oxide, peroxynitrous acid and nitric acid. All of these species have a strong oxidation potential. Relaxations of excited species to lower energetic states produce UV light emissions that also participate in degradation of organic molecules.

The first use of nonthermal plasma was in ozone production. Streams of air with ozone, after nonthermal plasma treatment, were introduced to treated water. Furthermore, in addition to ozone, discharges in the air produce many other reactive species such as OH·, O·, N·, H_2O_2, and others. All of these species are short lived and decay before ozone gets into the water. However, if the reactor is designed in a way that the electrical discharges take place in close proximity to the water surface, or just above the water level, some of these species may get into water and destroy the pollutants.

There are two approaches in nonthermal plasma used in water treatment: plasma within liquid and plasma in contact with liquid. Plasmas within liquids can usually be obtained with a high voltage electrical discharge between electrodes immersed in the liquid phase, where one of the electrodes is immersed in water and the other is isolated with some dielectric. Plasma in contact with liquids is usually generated above the gas–liquid interface and reactive plasma species are generated in the vapor phase in contact with the liquid.

Based on reactor construction and type of discharge there are three types of electrical discharges. In contact glow discharge electrolysis means that a continuous dc voltage of around 0.5 kV is applied to a thin wire anode in contact with the water surface, while the cathode is dipped in water and isolated from the anode through a porous glass. A sheath of vapor forms around the anode through which current flows as a glow discharge. In a dielectric barrier discharge reactor the electrical discharges take place between electrodes where at least one of the electrodes is covered with a thin layer of dielectric material, such as glass or quartz. Pulsed corona discharges utilize high voltage pulses. They use an asymmetric electrode pair, where the discharge develops in the high field region near the sharp electrode and spreads out towards the cathode.

DIELECTRIC BARRIER DISCHARGE REACTOR

Dielectric barrier discharge is based on the use of at least one dielectric barrier in the discharge gap with time varying voltages applied to the electrodes. Atmospheric nonthermal coaxial dielectric barrier discharge (DBD) plasma reactor (Figure 1.) was designed by Kuraica et al. for the treatment of various water solutions[5]. A cylindrical reactor was prepared with Pyrex tubes that had an internal diameter of 28.5 mm. The outer electrodes were made with aluminum foil, which was sealed on an outer glass tube. The inner electrode was a glass cylinder with a diameter of 20 mm that was silver-plated on the inside. In this reactor water forms a falling film that is in direct contact with the plasma. A sample flows up through a vertical hollow cylindrical electrode and flows down, thus making a thin dielectric film over the inner electrode. A barrier discharge is generated in air within a 3.5 mm gap between the dielectric and the water layer by applying a sinusoidal voltage of 19 kV on the peak. The thin layer of water is in direct contact with the plasma, and oxidative species are transferred from the plasma into the liquid phase, where the reactions with the pollutants occur, which is of great importance, especially for short-living active species. To increase the total flow of the treated solution, three discharges are connected in parallel. The plug-in power for this system of discharges was 180 W. After the treatment, the solution was collected in a reservoir at the bottom of the reactor. The collected solution was re-introduced through the reactor for the next treatment, when the total amount of solution from the previous run had already passed. The energy density (ED) of ~ 45 kJ L^{-1} was introduced into the solution with one pass through the reactor. A high voltage transformer was used as a power supply, which allows the variation of the sinusoidal voltage up to 20 kV. The frequency for the plasma reactor was set at the optimal value of 300 Hz. The total flow rate through three parallel DBD reactors was 210 cm^3 min^{-1}.

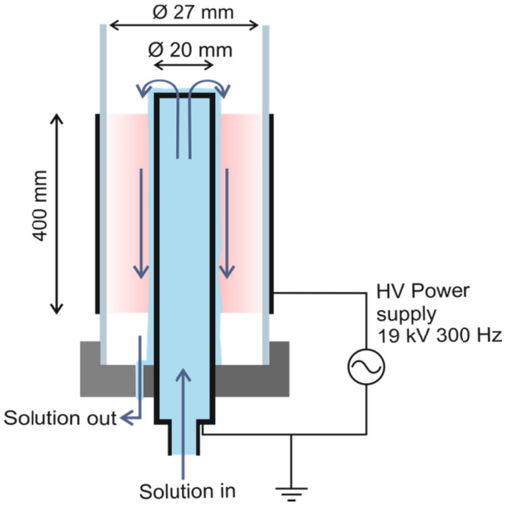

Figure 1. Scheme of water falling film DBD reactor used in experiments.

CHARACTERIZATION OF REACTIVE SPECIES GENERATED DURING WATER TREATMENT

For the formation of the hydroxyl radical and long-living chemical species (H_2O_2, O_3, NO_3^- and NO_2^-), generated in the liquid phase of a water falling film, dielectric barrier discharge dependence on the gas atmosphere (air, nitrogen, oxygen, argon and helium) was studied[6]. The chemical molecular probe dimethyl sulfoxide was employed for quantification of •OH, and the influence of the hydroxyl radical scavenging on formation of reactive oxygen and nitrogen species was investigated.

The hydroxyl radical concentration increases with increase of energy density (ED) (Fig.2). Production rate and G value, i.e. the energy yield, which is defined as molecules of the compound produced per 100 eV or grams per kWh, were determined.

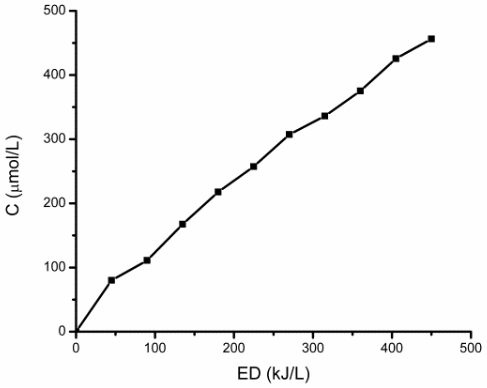

Figure 2. Production of OH radicals in the DBD reactor with different ED values

Hydrogen peroxide production in dependence on ED in distilled water and in DMSO solution was determined. Production of H_2O_2 increases with increasing energy density. The results obtained in DMSO differ significantly compared to those found in distilled water. The production of H_2O_2 formed by recombination of two $\cdot$OH radicals can be eliminated in DMSO solution, due to the fast reaction of DMSO and $\cdot$OH radicals. Also, a possible decomposition of H_2O_2 by $\cdot$OH is substantially reduced due to the mentioned reaction of DMSO and $\cdot$OH. Scavenging of $\cdot$OH by DMSO also indicates the role and impact of $\cdot$OH radical on the yield of H_2O_2 and other reactive species.

Dissolved ozone concentration measured in distilled water and in DMSO solution increases with energy density. In air, very low concentrations of ozone were formed when DMSO was treated in the discharge, reaching maximal values of 0.05 mg L^{-1}. Decrease of residual ozone during treatment of DMSO in air could be a consequence of several factors. For discharge in the air, higher concentration of nitrites was found in DMSO solution than in distilled water, which contributes to a decrease of ozone in DMSO solution due to consumption of ozone in oxidation of nitrites to nitrates. Further, it is possible that ozone reacts with DMSO, but this reaction is very slow compared to the reaction rate of hydroxyl radical with DMSO.

In air plasma formation of nitrite was observed with higher concentration in DMSO solution than in distilled water. In case of nitrates, highest concentration of nitrates was found in water treated in air, with notably lower values when DMSO solution was treated. Ozone and hydroxyl radical are consumed in reactions with DMSO and its degradation products, which suppresses the formation of nitrates in DMSO compared to water, since nitrates are mainly formed through oxidation of transient and primary nitrogen species.

Electrical discharges generated in air–liquid environments generate highly acidic conditions in water accompanied by an increase in solution conductivity, which are largely attributed to the formation of nitrous and nitric acids. Acidification and increase of conductivity due to plasma treatment can be observed in water and in DMSO solution (Fig.3). In the water treatment acidity is presumably governed by the nitrogen species, i.e. nitrates and nitrites. As nitric acid is a strong acid and nitrous acid is a weak acid, we obtain lower pH values in system air-water then in system air- DMSO solution.

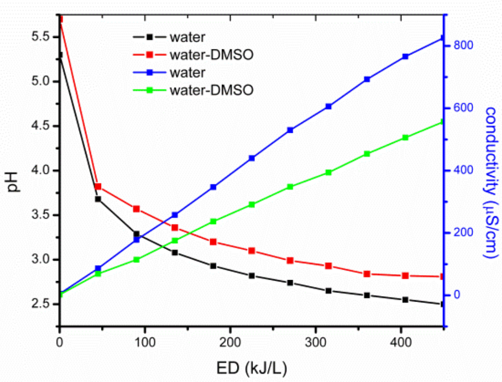

Figure 3. Changes of pH and conductivity in the DBD reactor with different ED values

DEGRADATION OF ORGANIC CONTAMINANTS

In order to examine efficiency of plasma reactor it was tested for degradation of different emerging organic contaminants. Among them we choose textile dyes, pesticides, pharmaceuticals and personal care products.

The textile industry with a consumption of over 7×10^5 tons of dyes per years is often considered as one of the major water polluters. Small amounts of dyes (<1 mgL^{-1} for some dyes) in the water, seriously affects the aesthetic quality and transparency of water bodies such as lakes, rivers and others. Light absorption diminishes photosynthetic activity of algae and seriously influence on the food chain. Azo dyes are major colorant in textile industry so the decolorization of four commercial reactive azo dyes C.I. Reactive Black 5, C.I. Reactive Blue 52, C.I. Reactive Yellow 125 and C.I. Reactive Green 15 was studied using a non-thermal plasma reactor based on coaxial dielectric barrier discharge (DBD)[7].

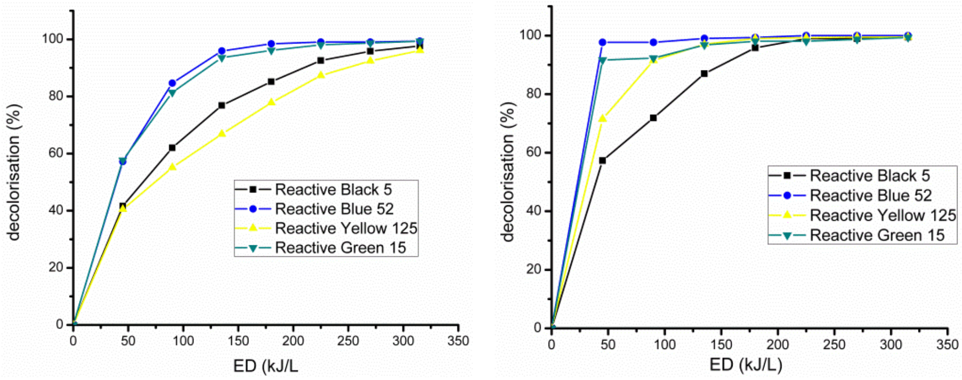

Figure 4. The change in decolorization of azo dyes in DBD reactor with different ED values after 5 min (left) and after 24 h (right)

After applied energy density of 315 kJL^{-1} high decolorisation degree (higher than 90 %) was obtained. It is interesting that we can distinguish two different kinetic for Reactive Black 5 and Reactive Yellow 125 on the one side and Reactive Blue 52 and Reactive Green 15 on the other side. First pair is more stable toward degradation (Figure 4). Initial pH value of tested solutions, has shown no influence on decolorization kinetics. In all cases decolorization after the first treatment (i.e. 45 kJ/L) measured 5 min after passing through the DBD reactor was 40–60%, while 24 h after the plasma treatment, decolorization has increased to 70–97%, depending on the dye . Ozone and hydrogen peroxide are the only oxidizers generated in the plasma, which are stable enough to react with the dye molecules outside of the plasma reactor so they are primarily responsible for the continued process of decolorization.

In order to get better yields in agriculture the use of pesticides continually increases. But some amounts of pesticides can get in the water reservoir during leaching from fields. Elimination of pesticides from wastewater effluents is the subject of considerable concern of environmental remediation and has attracted many researchers in recent years. Triketone class of herbicides, mainly mesotrione and sulcotrione are now frequently employed as atrazine substitutes in maize crops. Mesotrione is a relatively new member of the benzoylcyclohexanedione family of herbicides which is chemically derived from a natural phytotoxin produced by the bottlebrush plant *Callistemon citrinus*. Degradation of mesotrione and sulcotrione, as members of triketone group, using dielectric barrier discharge was done[8]. The results of the degradation were compared with other AOPs (Fenton reaction, ozonization and photocatalysis). The disappearance of the pesticides peak occurred after the tenth pass through DBD (introduced energy density of 450 kJ/L). Degradation products were identified by high performance liquid chromatography (HPLC–DAD) and UHPLC Orbitrap–MS analyses. Degradation products obtained in DBD reactors were identical with those in the ozonization and in Fenton reactions are identical with photocatalysis. In all cases aliphatic part cyclohexane-1,3-dione undergo oxidative opening of ring and quickly transforms into aliphatic carboxylic acids. Aromatic part was more stable toward degradation in DBD and ozonization. In Fenton reaction and photocatalysis degradation of aromatic rings was confirmed. These results suggest that dominant species responsible for the pesticide degradation in DBD reactor was ozone. The formation of ·OH radicals in plasma treatment was favored in basic conditions. Lowering of the pH could be an explanation for favoring of ozone as reactive species over ·OH radicals. In order to test the efficiency of the reactor in a real sample we tested degradation in Danube water. Natural waters are usually very complex systems and they contain a variety of organic and inorganic substances which may affect transformation of pollutants. Slower degradation (about 20 %) of sample in Danube water in DBD reactor was due to the presence of organic matter and inorganic ions which compete with reactive species formed during the degradation of pesticides.

Pharmaceutical residues have been detected frequently in the aquatic environment at very low concentrations (ng/L to μg/L). Nevertheless, due to designed persistence and biological activity their long-term presence poses real environmental risks. Ibuprofen (IBP) is a widely used non-steroidal anti-inflammatory drug (NSAID), consumed in high amounts in both human and domestic animal practices or farming. After excretion IBP leaves the body in the form of unaltered parent compound at 15% or as metabolized hydroxy-ibuprofen at 26% and carboxy-ibuprofen at 43% of applied therapeutic dose. Toxicological effects of ibuprofen metabolites (human or microbial origin) in the aquatic environment have been reported to influence cyclooxygenase (COX) reactions and therefore could affect not only the reproduction of aquatic animals, but also the photosynthesis of aquatic plants. Degradation efficiency of ibuprofen (60 mgL^{-1}) in the NTP reactor after applied energy density of 180 kJL^{-1} was 85% in DBD[9]. In case of ibuprofen DBD treatment gave better results in comparison with Fenton reaction. Nine degradation products were identified during DBD treatment: four aromatic compounds and five aliphatic carboxylic acids.

Surfactants are a group of compounds that are widely used in industrial, agricultural, and pharmaceutical markets in various products, including detergents, pesticides, petroleum products, cosmetics, and pharmaceuticals. Surfactants have a broad spectrum of applications because of their amphiphilic nature: they consist of a polar head group and a non-polar hydrocarbon tail and combine both hydrophobic and hydrophilic properties in one molecule. Non-ionic surfactants (alkylphenol polyethoxylates, APEs) display a low biodegradability and high toxicity. Degradation efficiency in case of Triton X-100[10], sodium-dodecylbenzensulphonate and lauril sulphate[11] was determined by the decrease in the absorbance of derivatized products (Cobalt thiocyanate method for nonionic surfactants and Methylene blue index for anionic surfactants). In all the cases concentrations of surfactants in solution were 100 mgL^{-1} and degradation efficiency were around 90 %. In case of Triton X-100 products of degradation were analyzed with mass spectrometry. Mass spectra confirmed that primary degradation begins at the ethoxy chain and the degradation of TX-100 in the DBD reactor occurs via shortening of the ethoxy chain.

INFLUENCE OF CATALYST

The catalyst in plasma treatment can influence the degree of degradation, energy yield (amount of substances degrade per amount of introduced energy) and mineralization efficiency. In order to improve results of plasma treatment different catalyst system were tested in all cases.

In the case of textile dyes the effect of plasma treatment can be significantly intensified with addition of hydrogen peroxide. For example, the most effective decolorization of 97% was obtained with addition of 10 mM H_2O_2 in a system of 80.0 mgL^{-1} Reactive Black 5 with applied energy density of 45 kJL^{-1}, after residence time of 24 h. Without the catalyst similar results can be obtained with 315 kJL^{-1} applied energy density. Further increase of hydrogen peroxide does not influence degradation efficiency. Also, the effect of plasma treatment can be enhanced with addition or iron salts if the conditions for Fenton reactions are fulfilled. After 24 h, at energy density 90 kJL^{-1} and higher, H_2O_2 which is produced in larger amounts, reacts with Fe^{2+} (1, 2 and 5 mgL^{-1}) thus contributing to the increase of decolorization by approximately 10%, compared to the system without Fe^{2+}. In this case, the energy saving was 45 kJL^{-1}.

In the case of mesotrione four different catalyst systems were tested (Fe^{2+}/DBD, Co^{2+}/DBD, Mn^{2+}/DBD and H_2O_2/DBD)[12]. For all catalysts the concentrations were optimized. Comparison of degradation efficiency for optimal concentrations of catalysts in each catalytic DBD systems and non-catalytic system was shown in Figure 5. All systems have proved to be successful in improving mesotrione degradation in DBD reactor, but the highest efficiency was achieved in system 5 ppm Fe^{2+}/DBD. Mn^{2+} and Co^{2+} catalytic systems gave the same degradation products and very similar degradation efficiency. Catalytic system 10 mM H_2O_2/DBD gave significantly different degradation products than other catalytic systems. This could be explained by the higher production of OH radicals, one molecule H_2O_2 gave two radicals. Additional amounts of radicals do not react with mesotrione but react with created degradation products which lead to higher mineralization efficiency.

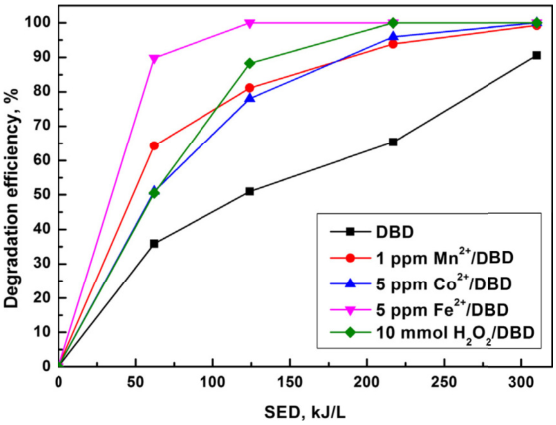

Figure 5. Degradation of mesotrione in presence of optimal concentration of catalyst

Degradation efficiency of ibuprofen in the DBD reactor after 15 min of treatment time was 85% in DBD and 99% in DBD/Fe^{2+}. During the first 10 min of treatment – for the same time (ED) – DBD/Fe^{2+} had 30% higher degradation efficiency. After 12 min the difference in degradation percentage between treatments decreased to 20% and after 15 min of treatment it was less than 20%, as the reaction in DBD/Fe^{2+} treatment reached a plateau. In the DBD/Fe^{2+} only four degradation products were identified. They were all aliphatic carboxylic acids. This means that the addition of a homogenous catalyst in the DBD reactor significantly improved not just the degradation, but also the mineralization rate. Therefore, the addition of a homogenous catalyst significantly influenced the efficiency of ibuprofen degradation in the NTP reactor.

In case of nonionic surfactants, two catalytic systems (Fe^{2+}/DBD and H_2O_2/DBD) were tested. Better results were obtained with iron as the catalyst. This system gave almost a complete removal of TX-100 (97%) for ED = 200 kJ L^{-1}. Without catalysts, similar degradation was obtained with applied energy density of 450 kJ L^{-1}. In mass spectra different products were observed compared with non-catalytic treatment. With catalyst products of aromatic ring hydroxylation and cleavage of the alkyl group were observed. In treatment of anionic surfactants catalysts affect only degradation of sodium dodecylbenzene sulphonate. Hydrogen peroxide had a greater impact on the degradation efficiency than iron (II) as a catalyst. The increase was about 30 % for the first four passes, while other passes showed an increase of about 10 %. In the case of iron, the increase was around 10 % for all the passes. For both catalysts, the final degradation (after ten passes through the reactor) increased by approximately 10 %. Catalysts have no influence on SDS degradation and we propose that reaction rate phase, in that case is hydrolysis of SDS.

MINERALISATION EFFICIENCY

The decreases of TOC value as a parameter of mineralization efficiency were monitored. DBD treatment generally shows low mineralization efficiency, measured as TOC value. It can be significantly improved with a catalyst. In case of mesotrione non-catalytic DBD treatment reduced TOC value by 34%. Catalytic DBD treatments gave higher TOC removal efficiency compared to non-catalytic DBD. Of all four used catalytic systems 10 mM H_2O_2/DBD gave the highest TOC removal (71%). Something lower efficiency was obtained with iron as catalyst (61 %). On the other hand Mn and Co gave similar results as system without catalyst. In ibuprofen treatment the DBD poorly reduced the TOC value (>10%) and the catalytic treatment (DBD/Fe^{2+}) had the TOC removal efficiency of 35%. Catalytic treatment show better removal efficiency than Fenton reaction in ibuprofen treatment. In the treatment of Triton X 100 the mineralization efficiency in the non-catalytic DBD treatment was very low (1%). The addition of the homogenous catalysts H_2O_2 and Fe^{2+} significantly improved the mineralization efficiency of TX-100. The catalytic system H_2O_2/DBD resulted in mineralization efficiency in the range of 4–34%, depending on the H_2O_2 concentration, whereas the Fe^{2+} /DBD mineralization efficiency was in the range of 2–21%, depending on the Fe^{2+} concentration. In the case of anionic surfactants better results in mineralization efficiency were obtained with iron as a catalyst.

EFFECT OF INORGANIC SALTS

In order to examine the influence of inorganic salts presence in wastewater from textile factories on degradation of textile dyes, three salts in different concentrations were tested[13]. The results indicated that decolorization of the dyes was significantly limited in the presence of the salts. Increasing the concentrations of inorganic salts in the water reduced the efficiency of decolorization of the dye, to varying degrees depending of the salt used. The most effective decolorization, of over 90 % was obtained with addition of 50 g L^{-1} NaCl with applied energy density of 135 kJ L^{-1} 24 h after plasma treatment. Decolorisation in the presence of the inorganic salts Na_2SO_4 and Na_2CO_3 was lower than the solution without salt. The increased decolorisation with addition 50 g L^{-1} NaCl was explained by the formation of hypochlorite from the chloride ions during the plasma treatment.

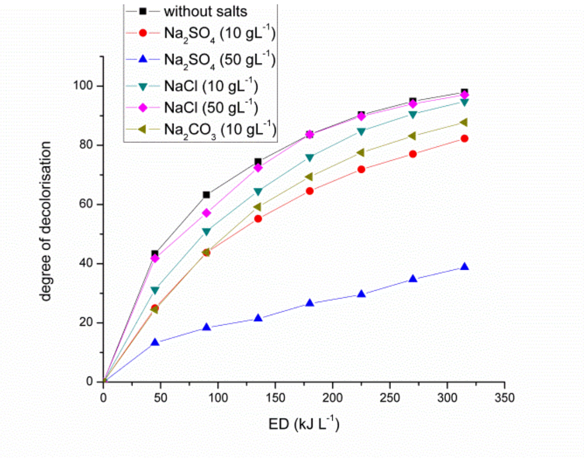

Figure 6. Effect of inorganic salts on decolorisation Reactive Black 5 solution

EFFECT OF ORGANIC COMPOUND CONCENTRATION

In order to examine the effect of contaminants concentration on degradation efficiency, five different concentration of Reactive Black 5 were tested. With the increase of concentration, degradation efficiency decreases, but the energy yield increases. Amounts of produced reactive oxygen species does not depend on the concentration of the compounds so a decrease of degradation efficiency could be expected. On the other hand in the presence of higher concentration of compounds, the possibility of reactive oxygen species quenching decreases, because effective collision with target compounds increases and that results in a higher energy yield.

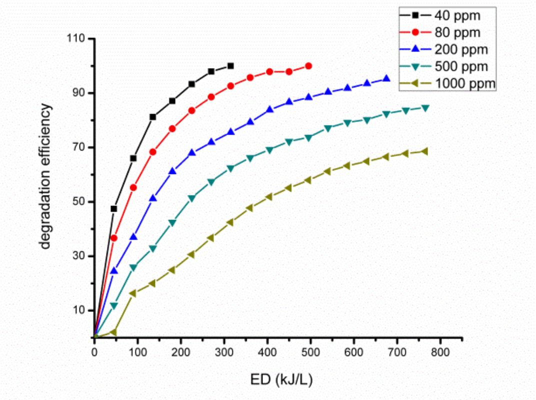

Figure 7. Effect of Reactive Black 5 concentration on degradation efficiency

TOXICITY TEST

For the toxicity screening test the brine shrimp *Artemia salina* was used. In treatment of textile dyes, toxicity tests have shown that toxicity of the dye solutions was reduced or maintained at the same level after the treatment, except for Reactive Green 15 where slight increase of toxicity was detected for only one concentration value. Products of pesticide degradation, according to the results of the toxicity test, could be considered low toxic to non-toxic. Similar results were obtained in ibuprofen degradation. When *A. salina* was exposed to the initial solution of TX-100 (100 ppm), the observed mortality was 76%. However, after the application of the DBD treatment, the toxic effect was reduced to 16% of mortality. The toxicity effect (%) of the initial solutions for anionic surfactants was higher in comparison to the treated solutions of SDS and SDBS in all the systems. In both cases, solutions treated in the non-catalytic DBD system and the catalytic DBD / Fe^{2+} system, induced lower toxicity in comparison to the catalytic system with hydrogen peroxide.

CONCLUSIONS

As we can see, nonthermal plasma is a promising technique for water treatment with high efficiency in different contaminants treatment. Results in treatments are comparable with other AOPs techniques. In plasma treatment combination of reactive oxygen species, shockwaves and UV light are used in treatment of contaminants. With homogenous catalyst, energy yield and mineralization efficiency can be significantly improved, but an effect of catalyst depends on structure of target compounds. Plasma treatment can be used in high loaded waters treatment. Products of degradation have lower toxicity than parent compounds. Disadvantages of plasma treatment are pH lowering, low mineralization efficiency and energy consumption.

REFERENCES

1. Long Wang, J., Jin Xu, L. (2012) Advanced Oxidation Processes for Wastewater Treatment: Formation of Hydroxyl Radical and Application, Critical Reviews in Environmental Science and Technology, 42(3), 251–325
2. Oturan M. A., Aaron J. J. (2014) *Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review,* Critical Reviews in Environmental Science and Technology 44(23), 2577-2641
3. Jiang B., Zheng J., Qiu S., Wu M., Zhang Q., Yan Z., Xue Q., (2014) *Review on electrical discharge plasma technology for wastewater remediation*, Chemical Engineering Journal, 236 348–368.
4. Hijosa-Valsero M., Molina R., Montràs A., Müller M., Bayona J. M., (2014) *Decontamination of waterborne chemical pollutants by using atmospheric pressure nonthermal plasma: a review*, Environmental Technology Reviews, 3(1), 71–91.

5. Kuraica M. M, Obradović B. M, Manojlović D., Ostojić D. R., Purić J. (2004) *Ozonized water generator based on coaxial dielectric-barrier-discharge in air* Vacuum 73 705–8
6. Kovačević V. V., Dojčinović B. P., Jović M., Roglić G. M, Obradović B. M., Kuraica M. M. (2017) *Measurement of reactive species generated by dielectric barrier discharge in direct contact with water in different atmospheres* J. Phys. D: Appl. Phys. 50 155205
7. Dojčinović B. P., Roglić G. M., Obradović B. M., Kuraica M. M., Kostić M. M., Nešić J., Manojlović D. D., (2011) *Decolorization of reactive textile dyes using waterfalling film dielectric barrier discharge*, *J. Hazard. Mater*, 192(2), 763–771
8. Jović M. S., Manojlović D. D., Stanković D., Dojčinović B. P., Obradović B. M., Gašić U. M., Roglić G. M., (2013) *Degradation of triketone herbicides, mesotrione and sulcotrione, using advanced oxidation processes*, *J. Hazard. Mater*, 260 1092–1099
9. Marković M., Jović M., Stanković D., Kovačević V., Roglić G., Gojgić-Cvijović G., Manojlović D., (2015) *Application of non-thermal plasma reactor and Fenton reaction for degradation of ibuprofen*, Science of The Total Environment, 505 1148–1155
10. Aonyas M. M., Nešić J., Jović M., Marković M., Dojcinović B., Obradović B., Roglić G. M., (2016) *Degradation of Triton X-100 in water falling film DBD reactor,* CLEAN - Soil, Air, Water, 44 (4), 422–429
11. Aonyas M. M., Dojčinović B. P., Dolić S. D., Obradović B. M., Manojlović D. D., Marković M. D., Roglić G. M., (2016) *Degradation of anionic surfactants using the reactor based on Dielectric Barrier Discharge (DBD*) J. Serb. Chem. Soc. 81 (9) 1097–1107
12. Jović M. S., Dojčinović B. P., Kovačević V. V., Obradović B. M., Kuraica M. M., Gašić U. M. and Roglić G. M., (2014) *Effect of different catalysts on mesotrione degradation in water falling film DBD reactor*, Chemical Engineering Journal, 248 63–70
13. Dojčinović B. P., Roglić G. M., Obradović B. M., Kuraica M. M., Tosti T. B., Marković M. D., Manojlović D. D. (2012 *)Decolorization of reactive black 5 using dielectric barrier discharge in the presence of inorganic salts* J. Serb. Chem. Soc. 77(4), 535-548

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MANAGING PROTECTED AREAS: NEW APPROACH TO PROTECTED AREA MANAGEMENT – THE ROLE OF THE LOCAL PEOPLE

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ABSTRACT

Protected areas are primarily viewed in biological or ecological terms, but they provide numerous functions beneficial to humans, and even essential to human welfare. Protected areas contribute to a country's social and economic objectives through supporting ecosystem services, promoting the sustainable use of renewable resources. However, protected areas can only deliver their environmental, social and economic benefits if they are effectively managed. Capacity to manage has many components and cannot be summarised in a single measure. The principal dimensions are the system of governance, level of resources, and community support. In order to adequately protect ecologically valuable areas, it is necessary to recognize the role of people in sustaining these systems and to engage people in protecting them. Participatory approaches have proved to be most successful in situations where the goals of the process are clear and there are positive attitudes towards conservation. The implementation of participatory approaches is proposed as a means of promoting sustainable resource use and helping to ensure the ongoing involvement of local people in conservation.

Key words: protected area, capacity to manage, local people, participatory approaches, sustainable resource use.

INTRODUCTION

Status of protected areas and management objectives

Around the world, protected areas are seen 'as a key to conserving natural resources on land and at sea' (21). According to the International Union for Conservation of Nature and Natural Resources (IUCN) definition of a protected area, namely is:
"*An area of land and/or sea especially dedicated to the protection and maintenance of biological diversity, and of associated cultural and natural resources, and managed through legal or other effective means* " (23).

The number and extent of the global network of protected areas has grown steadily throughout the 20th century most notably, as shown in figure 1, since 1970 (18). This indicates that governments are continuing to make efforts to establish new protected areas (18). After the establishment of Yellowstone, the first national park in the USA, in 1872, the concept of protected areas spread all over the world. According to the latest list of the United Nations compiled in 2014, there are 209,429 protected areas in the world today covering a total area of 32,868,673 square kilometres, larger in size than the African continent. A total of 3.41% of the world seas is under protection and 14% of the Planet's land surface (8).

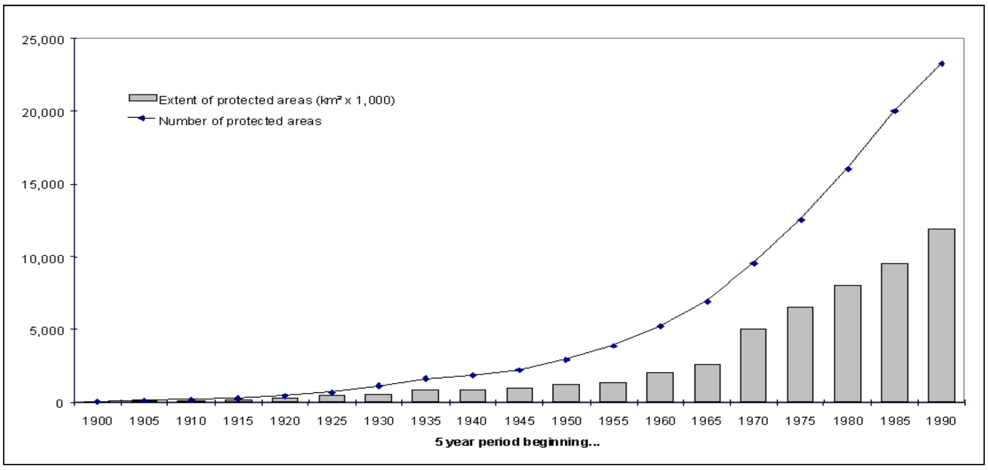

Figure 1. Cumulative growth in the number and extent of protected areas from 1900-1994 (18)

To help improve understanding and to promote awareness of the functions of protected areas, the IUCN has developed a six category system of protected areas identified by their primary management objective (23), as shown in table 1.

Table 1. IUCN management categories of protected areas (23)

Category	Description
I	Strict Nature Reserve/Wilderness Area: Protected area managed mainly for science or wilderness protection
Ia	Strict Nature Reserve: Protected area managed mainly for science
Ib	Wilderness Area: Protected area managed mainly for wilderness protection
II	National Park: Protected area managed mainly for ecosystem protection and recreation
III	Natural Monument: Protected area managed mainly for conservation of specific natural features
IV	Habitat/Species Management Area: Protected area managed mainly for conservation through management intervention
V	Protected Landscape/Seascape: Protected area managed mainly for landscape/seascape conservation and recreation
VI	Managed Resource Protected Area: Protected area managed mainly for the sustainable use of natural ecosystems

The IUCN protected area management categories system is based upon the primary objective of management. Tab. 2. shows how an analysis of management objectives can be used to identify the most appropriate category.

Table 2. Matrix of management objectives and IUCN protected area management categories (23)

Management objective	**Ia**	**Ib**	**II**	**III**	**IV**	**V**	**VI**
Scientific research	1	3	2	2	2	2	3
Wilderness protection	2	1	2	3	3	-	2
Preservation of species and genetic diversity (biodiversity)	1	2	1	1	1	2	1
Maintenance of environmental services	2	1	1	-	1	2	1
Protection of specific natural/cultural features	-	-	2	1	3	1	3
Tourism and recreation	-	2	1	1	3	1	3
Education	-	-	2	2	2	2	3
Sustainable use of resources from natural ecosystems	-	3	3	-	2	2	1
Maintenance of cultural/traditional attributes	-	-	-	-	-	1	2

Key: 1 = Primary objective; 2 = Secondary objective; 3 = Potentially applicable objective; – = not applicable

The data in table 2. shows that some recreation and tourism is likely to occur as a management objective in every category of protected area, with the exception of Category Ia (the strict nature reserve). Protected areas are established primarily to preserve some type of biophysical process or condition, such as a wildlife population, habitat, natural landscape, or cultural heritage, for example, a community's cultural tradition (tab. 2) (11).

The data also shows that biodiversity protection, though a critically important function of many protected areas is far from the sole purpose, and is frequently not the primary purpose of a protected area (11). It is, though, a requirement of the IUCN definition that any protected area should always have a special policy to protect and maintain biodiversity.

Protected areas are primarily viewed in biological or ecological terms, but Dixon & Sherman (10) emphasised the economic importance of land managed for conservation objectives. However, protected areas are important at many levels, from local and national to global levels, and they carry out numerous functions beneficial to humans, and even essential to human welfare. Ten important functions of protected areas are listed in table 3 (35). The manner in which these functions are transformed into benefits for the affected populations will depend on the management objectives of the protected area and how effectively these objectives are converted into actions. Table 3 presents a model of the various scales at which benefits are delivered by these functions, ranging from local to global. The range of possible benefits at each scale indicates the importance of defining objectives for individual protected areas; different management approaches will provide different mixes of benefits at different levels[1] (35).

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[1] Protected areas provide benefits to people at all levels. Using the ten critical functions listed in the text, this table provides a model of the scale at which benefits can be derived, from 0 (= no benefit) to 4 (= maximum benefit). More precise determinations can be made for individual protected areas or for national protected area systems.

Table 3. The scale at which benefits are delivered by protected area functions (35)

	Scale at which benefits are delivered		
Key functions	**Local**	**National**	**Global**
1. Biodiversity	0-4	2-4	4
2. Watershed protection	4	2-4	1-3
3. Storm protection	4	2-4	1-3
4. Tourism	0-4	4	2
5. Local amenity	2-4	1-2	0-1
6. Forest products	0-4	1-2	1-2
7. Soil	0-4	1-2	1-2
8. Carbon	0-1	1-2	2-3
9. Research	0-3	2-4	2-3
10. Cultural values	0-4	2-4	1-2

The importance of protected areas is emphasised by international conventions and programmes such as the Convention on Biodiversity (CBD), the World Heritage Convention (WHC), the Ramsar Convention on Wetlands, the UN Law of the Sea Convention, UNESCO's Man and the Biosphere (MAB) Programme of the United Nations Educational, Scientific and Cultural Organisation (UNESCO) and the global programme of the WCPA. Together these agreements and programmes are the backbone of international policy on the establishment and management of protected areas for biodiversity conservation and the sustainable use of natural and cultural resources (40). The Convention on Biological Diversity marked a significant shift in the perception of protected areas by governments. It linked protected areas to larger issues of public concern, such as sustainable development, traditional knowledge, access to genetic resources, national sovereignty, equitable sharing of benefits, and intellectual property rights. Furthermore, since the adoption of the Convention on Biological Diversity (hereafter CBD), and because of Article 8a in particular, much greater emphasis has been placed upon the idea of developing national *systems* of protected areas as a means of conserving biodiversity *in situ* and for other purposes. Indeed, many protected areas now form part of international networks, both global systems, notably World Heritage sites, Ramsar sites and Biosphere Reserves; and regional systems, such as Natura 2000 network of nature conservation sites in Europe. There are calls to recognise fully the role of indigenous peoples with respect to protected areas (2).

Protected areas contribute to a country's social and economic objectives through supporting ecosystem services, promoting the sustainable use of renewable resources, as well as providing places for tourism and recreation (22). The constituency for protected areas is therefore broad and diverse. However, protected areas can only deliver their environmental, social and economic benefits if they are effectively managed (21).

The key questions of interest at the global level are whether the responsible authorities have the capacity to manage their protected areas effectively, and whether desired outcomes are being achieved on the ground. Capacity to manage has many components and cannot be summarised in a single measure. The principal dimensions are the system of governance, level of resources, and community support (figure 2). The measurement of these dimensions is contextual. What is effective legislation in one country may be entirely inappropriate in another with different legal and social systems. Similarly, it is only possible to assess the adequacy of resources for management in the context of some estimation of management needs (21).

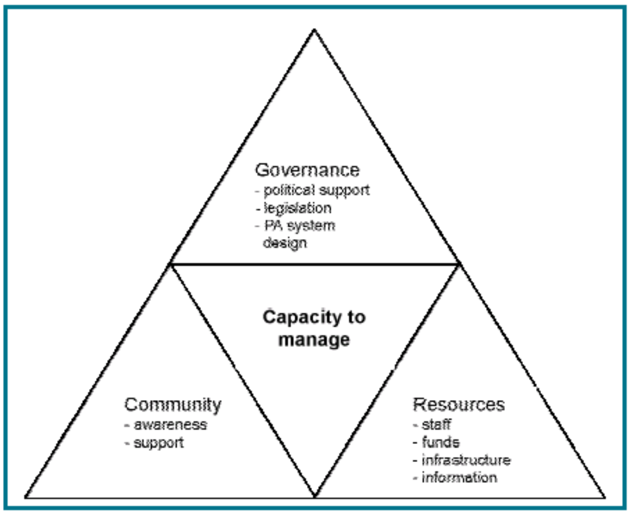

Figure 2. The dimensions of 'capacity to manage' (21)

Beyond such questions relating to the way in which protected areas are managed, the international community is even more interested in the outcomes of such management, i.e. the impact 'on the ground'. Issues such as the impact of protected areas on the conservation of biodiversity, and on other natural and cultural heritage resources, are of great concern. In this paper, however, the focus is on the role of local communities in the management of protected areas with the expectation that without the cooperation and assistance of local communities, achieving biodiversity conservation in places where the land and resources are fundamental to supporting people's livelihoods will be less successful than if the local people actively support this goal.

New approach to protected area management – the role of the local people

Historically, the creation of most protected area involved the exclusion of local people from almost any kind of access or use of the area (16). In the United Kingdom, for example, the tradition of exclusory Royal Forests meant that the leading conservationists were foresters from the Imperial Institute of Forestry at Oxford as well as biologists, zoologists and other natural science disciplines and their management philosophy emphasized that 'the public good was best served through the protection of forests and water resources, even if this meant the displacement of local communities' (31). People were not allowed to live inside the protected area or to use the area for extractive purposes (25). This exclusionary approach continues today, as or example, in a very large area earmarked for conservation in Costa Rica that is under a strictly protected regime that excludes local communities (6).

Denying local people the right to use these resources severely reduces their inclination to support conservation and often undermines local livelihood security (42). At the root of the relationship between indigenous groups and local communities with national governments and their conservation policies lies a combination of historical, cultural and socio-political factors. The important issue is the *"willingness of governments to recognise that local communities are vital actors in the delivery of conservation objectives. Governments that have not already done so, need to move from an implicit assumption that they manage against local communities to one where they recognise that protected areas should be managed for, with and often by local communities"* (4).

Property rights are a key social institution for allocating human access to land and natural resources. All societies have systems of land tenure – who has access to what, when, where, and sometimes, how – that allocate rights to public and private purposes. One defining characteristic of an indigenous culture is a traditional tenure system that defines the rules and responsibilities for relationships between people and the natural world (34). Tenure systems – upon which responsibility is built – are based on legitimacy drawn from the community in which they operate, rather than from the nation or state in which they are located. Indigenous systems of resource tenure are extremely variable, complex mixtures of individual and community rights, enforced by the local culture. However, the variation in resource management is part of an ongoing process to which the different interests and struggles of the various participants contribute (34).

In many European countries, including Germany (6) and France (14), the long established order of land tenure and rights of access to resources has generally been respected in recent decades. In Britain conservationists accepted the vision of nature as part of a process of 'continuity and gradual change, with man at the centre and integral to rural landscape'. British National parks thus recognized existing rights and sought to maintain the established patter of farming and land use by rural communities (16).

Recalling that protected areas have grown in number in the last decades, this necessarily means that many protected areas have been established in areas traditionally inhabited by humans (38; 55). In Latin America 86% of the existing protected areas have been established in areas currently inhabited by people; world-wide the figure is approximately 70% (16).

In this situation, the question of local people's position *versus* protected areas has become a highly relevant and widely discussed issue (16). Already in 1976 UNESCO, through its Programme on Man and Biosphere (MAB)[*], proposed the creation

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[*] The UNESCO-MAB World Network of Biosphere Reserves is one way of involving people in biodiversity conservation. The biosphere reserve approach links ecology with economics, sociology and politics, and ensures that good policy intentions do not yield inappropriate results. Biosphere reserves are indeed special places for people and nature, and a key help in managing our biosphere. Biosphere reserves are areas of terrestrial and coastal ecosystems promoting solutions to reconcile the conservation of biodiversity with its sustainable use. They are internationally recognized, nominated by national governments and remain under sovereign jurisdiction of the states where they are located. They serve in some ways as 'living laboratories' for testing out and demonstrating integrated management of land, water and biodiversity, which is the embodiment of the ecosystem approach' being developed by the Convention on Biological Diversity.

In short, biosphere reserves are much more than just protected areas. They represent a means for promoting management essentially as a pact between the local community and society as a whole (50).

of a biogeographically representative network of Biosphere Reserves in the sites of worldwide significance. In this case, the inhabitants of protected areas were for the first time taken into account, as the MAB-programme emphasized human beings as 'an integral part of the ecosystem and recognized the necessity of involving local inhabitants in conservation activities' (45). This perception was strongly emphasized some 15 years later, when the IV IUCN World Congress on National Parks and Protected Areas pointed out that the view of protected areas as islands apart from the surrounding areas and neighboring human communities should finally be left aside (33). Consequently, the Congress took the phrase "Parks for Life" as its slogan, and urged the governments to recognize 'the needs and aspirations of the people living in and around the protected areas, as well as to take appropriate measures in order to ensure that the local communities were not disadvantaged by protected areas '. This human dimension of biosphere reserves makes them special, since the management of a biosphere reserve essentially becomes a 'pact between the local community and society as a whole' (50).

In recent years several researchers have stressed the role of the local people in the successful management of protected areas. According to WELLS & BRANDON (55), there is a growing recognition that the sustainable management of protected areas ultimately depends on the co-operation and support of the local people. Similarly, KOTHARI *et al.* (29) argue that a protection strategy that alienates local communities from conservation is not only unjust to human rights but also harmful to conservation. Therefore, it order to achieve sustainable conservation, state legislators and environmental planners should involve local people in management of protected areas and *"need to identify and promote social processes that enable local communities to conserve and enhance biodiversity as a part of their livelihood system"* (33; 41).

Participation

The issue of participation is an important issue in protected area management. For instance, the IV IUCN World Congress on National Parks and Protected Areas called for increased community participation and human equity in the decision-making of protected areas in order to improve their management (22). The term *participation* can be interpreted in very different ways, and therefore it is essential to define it carefully (49).

Until the 1970s, the participation of local people in conservation was often seen as a tool to achieve the local approval to protected area plans, and participation was almost a mere public relations exercise. During the 1980s, participation of the local people was regarded as a mechanism to gain better results in natural resource protection, while in the 1990s, participation has been interpreted more and more as a means to involve local people in protected area management (41).

It is now widely assumed that participation is required in order to achieve sustainable and effective conservation, particularly in protected areas; that it can bring economic and social benefits to marginalised groups; and that devolution of decision-making will benefit biodiversity. 'Participatory approaches provide opportunities for the poor to contribute constructively to development' (12). The FAO People's Participation

Programme believes that 'participatory approach is an essential part of any strategy and its call for 'the active involvement and organization of grass roots level of the rural people' (12).

As sustainability is defined in ecological, economic, and social terms, participation, as a democratic means of decision-making, has been increasingly recognised 'as an essential means and end to the development of the social dimensions of sustainability' (15).

According to FINGER-STICH & FINGER (15), 'participation' is defined as, *"the voluntary involvement of people who individually or through organised groups deliberate about their respective knowledge, interests, and values while collaboratively defining issues, developing solutions, and taking – or influencing – decisions"*. Furthermore, defining who can participate will lead to different types of participation processes. FINGER-STICH & FINGER (15) distinguished three main types of participation: public participation, representative participation and community participation. This research focuses is on community-based participation processes. Public participation[2], collaborative management[3], and community-based management as types of participation may not always be distinct. 'They may be complementary and evolve into one another over time' (15). For example, a protected area policy may be drafted in consultation with the general public at the regional and/or national level, then there may be a co-management body to monitor the management of a particular protected area, and it may work in partnership with community-based associations to adapt this management to particular places, activities, and social groups (15).

In order to understand the meaning of participation, as well as participation processes, the following definitions and understandings are collected from different authors.

Participation processes, whatever their type, have the potential to evolve and provide space and opportunities for social learning (28). Participatory theories, such as social forestry (27), emphasize policy-making based on direct citizen participation, ahead of expertise and citizen preference structures. These theories propose a restructuring of institutional arrangements to accommodate greater citizen deliberation. In the field of social forestry, KORTEN (26) identified several weaknesses in early traditional community development programmes, which he attributed partly to inappropriate governance structures. He maintained that new arrangements can be achieved through *"innovative social learning (which emphasizes) central facilitation over central control, performance monitoring and self-correction over planning, encourages local initiative and self-control, and reflects a tolerance for the ambiguity and uncertainty inherent in the learning process"* (27).

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[2] Team of specialists (FAO/ECE/ILO,(21)) Public participation defined as, *"a voluntary process whereby people, individually or through organised groups, can exchange information, express opinions and articulate interests, and have the potential to influence decisions or the outcome of the matter at hand"* (13).

[3] Collaborative management or '**co-management'** is defined as *"a situation in which two or more social actors negotiate, define and guarantee amongst themselves a fair sharing of the management functions, entitlements and responsibilities for a given territory, area or set of natural resources"* (5). Co-management (short for collaborative or joint management) – this term has been defined as, *"...durable, verifiable and equitable forms of participation, involving all relevant and legitimate stakeholders in the management and conservation of resources"* (3).

"While understanding that all participatory processes entail communicative action, it is useful to recognise that in the situation where problems are being defined and actors are forming or changing their roles, the essence of the participatory process is communicative action. This means that the degree of instrumental or strategic policy development is low since there is not a clear public problem and no organised social interests. Indeed, one can expect this part of the policy process to possibly extend over years as the nature of the public problem is slowly understood and shared understanding emerges through dialogue between the actors'' (46).

Thus, communicative action leads to a better understanding of the actors, stakeholders and interests and why they are associated with this problem (15).

"Participation processes are both a way to manage conflict by seeking compromise between various interests, and they are also a means of developing more creative solutions that would not have emerged without the interaction of stakeholders. The decisions born out of such collaborative thinking and negotiation have the advantage of being the product of all those taking part, and are therefore more likely to be effective. Effective participation is a means and an outcome of collaborative learning'' (15).

In general, scholars have agreed about main point of participation, namely: learning process, communicative action and participation is a means and an outcome of collaborative learning.

One promising overall approach to building cooperation between local people and protected area managers is through 'collaborative management' or 'co-management' of protected areas – a partnership whereby various stakeholders agree to share amongst themselves the management functions, rights, and responsibilities for a territory or set of resources under protected area status (3).

In recent years, there has been a growing interest in the integrated management of protected areas, which means the ample participation of the local people in the decision-making and management of the area (16; 38; 49). PIMBERT & PRETTY (41) classify the different levels of participation in protected area management as follows (tab. 4).

Table 4. A typology of participation (Adopted from PIMBERT & PRETTY,(41))

	Passive participation
2	**Participation in information giving**
3	**Participation by consultation**
4	**Participation for material incentives**
5	**Functional participation**
6	**Interactive participation**
7	**Self-mobilization**

In this table, *passive participation* means informing the stakeholders on what has happened in the area, or what is going to take place, while their reaction concerning the information or the activities realized are not taken into account.

Participation in information giving means that information about the protected area is gathered from the local inhabitants through surveys, but people do not have the opportunity to influence the proceedings in the area. This way their role in the participation is only to give information. Discussing the results more widely, and people's *participation by consultation* in the definition of the problems and in the search for solutions of the management of the area is a step further in local participation. But even in this case they do not have an active role in decision making, led by professionals. Sometimes participation means local *participation for material incentives* in which case local people provide some of their resources such as labour, land or collecting genetic material in return for food, cash and other material incentives. In these cases, participation often finishes when the incentives end (41). However, compared to the first two levels, this kind of participation offers the local people a role as a subject, and not just an object of activities, as they both give and receive something from the protected area authorities.

According to PIMBERT AND PRETTY (41), only the last three levels of participation (functional, interactive and self-mobilization) are sufficient in order to achieve effective, efficient and sustainable conservation in protected areas. *Functional participation* is defined as people participating by forming groups to meet the predetermined objectives related to protection of the area. This kind of participation can also include the promotion of externally initiated social organizations. Even though these organizations are usually dependent on external facilitators, they may later become more independent. In *interactive participation* people formulate a joint analysis, which leads to action plans and to the formation of new local groups and the strengthening of the existing ones. These groups then take control over local decisions. Finally, self-mobilization means people taking initiatives, independent of external institutions, to change the management systems of the natural resources (41).

Sustainable protected area management requires, first of all, understanding of the complex ecological and social relationships in rural areas, and valuing of local people's ideas and knowledge systems. Both the conservation authorities and the people living in and around protected areas have their particular strengths and limitations. For this reason, the advantages and skills of professionals need to be combined with the strengths of local people, this kind of participation process, at its best, leading to the real empowerment of the local people (41).

Participatory forest management

Forests and trees can make a significant contribution in sustainable livelihoods. It has been estimated that about 1.6 billion people worldwide are heavily dependent on forest resources for their livelihoods. Within a local community, it is common to find that it is the poorest households, with less agricultural land, livestock, or labour are the predominant collectors of forest products (53). Despite the importance of forest resources to the poor, until recently efforts in development, as well as in forestry, have not paid sufficient attention to how natural capital, such as forests, is used in combination with other assets to sustain livelihoods. This has resulted in gaps in our understanding of the forests' contribution to sustainable livelihoods (9).

Forests are an important source of natural capital and provide non-material goods that contribute to livelihoods by enhancing social and human capital. Forestry initiatives supporting access to resources, participatory decision-making and equity assist in increasing well-being, especially that of the poor (54).

However, sustainability of the natural resource base is a critical concern of (and basis for) sustainable livelihoods. Increased sustainable use of natural resources can have a direct impact on the improvement of natural capital. The holistic approach of current sustainable livelihood initiatives recognises the vulnerability of the poor to resource degradation and promotes sustainable resource management as a critical element for sustainable improvement in the livelihoods of the poor. A key challenge lies in implementing environmental policy. One of the greatest needs may be for a policy and legal framework that legitimises participation in the co-management of the resources and incorporates multiple objectives, including poverty alleviation, and provides operational mechanisms (54).

Furthermore, meeting the needs of local people should be the principal objective of forest management, and this should be reflected in control and tenure arrangements (39). Poverty-oriented forestry is concerned with reducing the vulnerability of the poor by enabling people to continue to have access to the resources and product flows needed for subsistence purposes (54). A detailed assessment needs to be prepared by, or at least with the people concerned, in order to identify the complete range of relationships between the people and forest that they use and/or manage, the current limitations to their livelihoods and the potentials and desire for change. Experiences in community-based forestry demonstrate that a people-centred approach is viable and effective (54).

Some conservationists recommend participatory forest management over community or state forest management because participatory forestry enhances collaboration and understanding between forest communities and state authorities (e.g. 37; 45). However, POFFENBERGER & SINGH (44) and CAMPBELL *et al.* (7) warned that implementation of participatory forestry can be difficult, particularly where securing representation on joint management committees and reaching consensus on issues such as distribution of benefits to communities are concerned. GRUMBINE (19) and JACOBSON (24) suggested that these issues can partly be overcome if resource users and managers are aware of the forest management goals and practices, and have positive attitudes towards conservation. Furthermore, in protected areas, received benefit from tourism is a key factor for a local population to perceive conservation positively (see for example 52).

A correlation between benefits and positive attitudes has been confirmed in many cases (36; 49). Furthermore, literature based on empirical evidence indicates that three important refinements must be added to the statement claiming that benefit sharing contributes to cooperative attitudes towards conservation. These can be summarised as 1. the importance of economic viability from the local perspective (47), 2. an explicit link with long-term conservation interests, and 3. the need for proper institutional arrangements (1).

The attitudes and perceptions of the stakeholders towards a conservation area and the policy being implemented are an important element of sustainable conservation, and local communities must be actively involved, and their needs and aspirations considered if biodiversity conservation is to be successful. These trends have encouraged the development of a new conservation paradigm, 'community-based conservation', emphasising management of biodiversity by, for, and with local communities (56; 17).

All policies and programmes implemented under the community-based conservation paradigm share the key assumption that biodiversity conservation will only succeed if local communities receive sufficient benefits, participate in management, and therefore, have a stake in conserving the resource (17).

Examples of protected area management in the world - with an emphasis on participatory management

1. Nepal

The 7,683 km2 Annapurna Conservation Area is one of the most geographically and culturally diverse conservation areas in the world. About 118,000 people, mostly poor rural farmers, live in the region. Over 45,000 foreign trekkers visit each year, which has led to the development of hundreds of lodges and tea several years. While tourism has become important to the local economy, it has also led to serious environmental problems. Forests have been cleared to provide fuel for cooking and heat for visitors. Expanding agriculture,water pollution, poor sanitation and litter on trekking routes have all accelerated, compounded by a rapid growth in the resident population. The Annapurna Conservation Area Protect (ACAP) was initiated to help the inhabitants maintain control over their environment. An entry fee to Anpurna *Conservation* Area has been collected from tourists since 1989. The community benefits from increased control over tourism and revenue generation for community development projects such as bridge and trail repair, agricultural extension, and women's programs. Area committees monitor and help manage environmental resources and environmental education and tourism education programs are included in the schools and elsewhere (48).

2. India

This is another example of local participation in the management of natural resources. In fact, in the last ten years the way to manage the forests of India has drastically changed in relation to the management in the past one hundred years when the commercial use of forests was taking place. The problem of violating forest ecosystems and irresponsibility of local communities was highlighted in the National Forest Policy of 1952 (51).

The program where the community manages the forests is in action in the Haryana area, the lower Himalayas, which presents the most environmentally degraded region due to uncontrolled logging and grazing in the past. In the 1970s, the local population, Sukhomajiri people, took responsibility for the poor state of the environment in which they live while trying to find alternative sources of livelihood in order to reduce their dependence on the forest. They encouraged the regeneration of vegetation by using feed. Other villages in the area followed their example. The program has encouraged communities to protect and manage forests on a sustainable basis for their own benefit. This management style has led to an increase in revenues at the household level. Local forest management resulted in an improvement of wood and grass cover in forested areas, which also led to the improvement of soil moisture, the reduction of sludge loading and the reduction of watershed drainage, which consequently led to the reduction of flood occurrences (51).

3. Australia

In Australia, strong co-management arrangements for protected areas have been developed over the last twenty years, following legislation that recognised Aboriginal rights to land and natural resources. In 1981, Gurig National Park became the first jointly managed National Park in Australia; since then, further co-management arrangements have been developed for other parks in various states and territories, according to several models. Co-management represents a trade-off between the rights and interests of traditional owners and the rights and interests of government conservation agencies and the wider Australian community. In the most sophisticated arrangements, land ownership is transferred to Aboriginal people in exchange for the peoples' agreement that the area will remain under protected status as a national park for the foreseeable future and that responsibility for park management will be shared. The most recent form of protected area established voluntarily on existing Aboriginal-owned land - the Indigenous Protected Area is even more advanced in terms of self-determination and self management by the Aboriginal owners (5).

4. South Africa

South African National Parks (SANParks) is the leading conservation authority in all national parks around this country, responsible for 3 751 113 hectares of protected land in 20 national parks. The focus for SANParks in the first decade of democracy has been to make national parks more accessible to tourists in order to ensure conservation remains a viable contributor to social and economic development in rural areas (30).

The first board of South African National Parks was appointed in 1926. With the changed structure of the country after 1994, and with majority rule, the then National Parks Board re-conceptualised its role in South African society. SANParks, supported by the government through the Department of Environmental Affairs and Tourism has also increased the area of land under its protection by 360 000 hectares in this time (30).

Late last century, SANParks grew into one of the three largest players in the tourism industry in South Africa, and the largest in ecotourism or nature-based tourism, with in excess of 5200 beds and a further 1000 campsites. Having many of the best natural areas under its management and control, SANParks had a significant influence on development of the entire industry. However, in 1999 SANParks reviewed its commercial operations and found delivery of tourism products, often mediocre service standards and poorly rationalized pricing structure (30). This led SANParks to develop a Commercialization as a Conservation Strategy, which aimed to generate additional revenue in order to better conserve South Africa's protected areas; provide a foundation and regulatory framework for tourism; and transfer management of commercial operations to private sector operators. A key component of the strategy has been to let concessions in areas such as Kruger National Park for the provision of tourism service.

The primary objective of the concession process was to generate more revenue for the organization, processes were designed to encourage partnership that exhibited the correct mix of financial strength, requisite experience and strong empowerment credentials. The focus of empowerment was on promoting and providing business opportunities for historically disadvantaged entrepreneurs-in particular, those from local communities living adjacent to national parks (30).

5. Vietnam

Systems of protected areas in Vietnam are still being developed in terms of coverage and institutional arrangements. Over the past few decades, there have been a series of attempts to categorize Vietnam's protected areas and the government of this country prudently relies on the IUCN classification system. However, there is a lack of clarity in the way in which categories are presented which led to confusion. When it comes to establishing protected areas, the example of Vietnam shows us the way in which a great attention was given to the common language by explaining the concepts of categorization of protected areas and their modification in accordance with the needs of the country. A team of experts worked on translating and adapting the categories defined by the IUCN, but in such a way that these translations are accurate and relevant in the local context (48).

In the beginning, the protected areas in Vietnam were only defined and their management was reduced to a literal translation. Also, the protection that existed was not in line with sustainable development. Local communities were forced to leave the protected areas and had no part in managing national parks or other categories of nature protection. One of the problems which is characteristic not only for Vietnam, leading to this kind of understanding of protected areas, is the lack of understanding and inadequate translation into the local language(48).

The Government of Vietnam is committed to the protection of biodiversity in the country and is one of the signatories of the Convention on Biological Diversity. Accordingly, it established a significant number of protected areas, some of which are of global importance. Systems of protected areas in Vietnam are still under development in terms of coverage and institutional arrangements. Currently, protected areas declared by the government include primarily "forests for special purposes", such as Xuan Thuy Wetland National Park. There are also four UNESCO nature reserves – The man and the Biosphere (*Can Gio mangroves*, *Cat Tien National Park, Red River Delta and the Cat Ba National Park*) and *Ha Long Bay* and *Phong Nha-Ke Bang National Park*, which are part of the World Natural Heritage. Existing protected areas include mostly forests, but some wetland and coastal areas are also under protection (48).

6. United Kingdom

The North York Moors National Park, a Category V protected area in the United Kingdom that includes land that is settled and has been farmed for millennia. The landscape encompasses large areas of semi-natural vegetation, such as ancient woodlands, interspersed with grazing areas, hedgerows, farmland, and some small towns and villages.

The relationship between the park and the local people is so close that the Park Management Plan is included as part of the general plan of Town and Country Development, prepared with the extensive involvement of the public. In fact, the majority of the North York Moors is under private ownership (a factor common to many other protected areas in Europe) and the management plan is therefore dependent on the cooperation of the landowners.

While building and engineering works are controlled in part by the Park Authority (normally without compensation), farming and land management activities generally remain outside their control. To ensure that farming and land management activities conform to the park plan, agreements are often signed between the landowners and the Park Authority. Though considered to be legally binding contracts, these agreements are entirely voluntary, although the Park Authority provides financial incentives and compensation in return for agreed works or management practices (5).

7. **Ecuador-**Galapagos Marine Reserve

Located approximately 1,000km from the Ecuadorian mainland, the volcanic Galapagos Islands contain remark able terrestrial and marine ecosystems and became, some years ago, the focus of complex and sometimes violent multi-stake holder conflicts. The rapid economic and demographic change, the presence of unregulated industrial fishing, the appearance of high-value fisheries for Asian markets, the state-imposed policy and regulations and the general non-compliance with the management plan of the Marine Reserve were all factors fuelling those conflicts. In 1998, in response to national and international concern about the threats facing them, Ecuador passed innovative legislation through a Special Law that, amongst other measures, introduced the control of migration within the country, created one of the largest marine reserves in the world (c.130,000 km²), prohibited industrial fishing and established instituitions for participatory management of the Marine Reserve. The creation of the Galapagos Marine Reserve was the fruit of a local exhaustive participatory planning process, which took two years 74 meetings of a multi-stakeholder planning group called Grupo Núcleo, two fisheries summit meetings and three community workshops) and produced a consensus management plan. The implementation of this plan, through a legally based participatory management regime, has been in progress now for several years (20).

8. Bolivia

The Kaa-yalya National Park (83.4 million hectares) is the largest in Bolivia and contains the world's largest area of dry tropical forest under legal protection. Another unique characteristic of this park is that it was created in response to demands for territorial recognition by the Guaraní Izoceño people. This is the first protected area in the Americas to be declared at the behest of the indigenous people, and it is the only park in the Americas where an indigenous peoples' organization (CABI-Capitanía del Alto y Bajo Izozog) has primary administrative responsibility. The Park's Management Committee comprises staff of the Ministry of Sustainable Development and Planning and representatives of CABI, WCS (a foreign environmental NGO), local municipalities, a community group of Chiquitanos, the Ayoreo Communityof Santa Teresita and the group of women of the Izozog indigenous communities. The indigenous representatives are the majority in the Committee, which is in charge of several management policies and decisions (5). In 1993, the new Agrarian Reform Law recognised Bolivia as a multi-ethnic and multi-cultural country, allowing for community land ownership and legalising the creation of indigenous territories (Territorio Comunitario de Origen - TCO) (5).

9. Canada -Gwaii Haanas: a successful example of co-management from Canada

In the Haida language, gwaii haanas means "islands of wonder and beauty". The Gwaii Haanas National Park Reserve, located within the Queen Charlotte Islands off the coast of British Columbia, was established in 1986 under an agreement between Parks Canada and the Council of the Haida Nation. The Haida themselves initiated the process, after their land and culture started to disappear due to heavy logging in their traditional territories. Through alliances with conservation organizations, the Haida people drew international attention to the spectacular beauty and diversity of their homeland and the need to protect it. The dual Park-Reserve status stems from the land ownership dispute. Both the government of Canada and the Haida claim ownership of the land. Fortunately, both sides have been able to put aside their differences regarding ownership and promote instead their common interests and goals. The Haida intent is to protect the area from environmental harm and degradation and continue traditional resource uses. The federal government's intent is to protect the area as a natural cultural environment as part of the national protected area system. Such objectives are perfectly compatible, leading to a relationship based on respect, reciprocity, empowerment and effective cooperation. In fact, Gwaii Haanas is now governed by a joint Management Board, made up of two Haida representatives and two Parks Canada representatives, working by consensus. This may slow down some decisions but assures that they are all well thought out and widely accepted (5).

10. Italy

One of the protected areas in Italy is the Etna Regional Park with an area of 59,000 ha. This park, which surrounds the active volcano Mount Etna, is the first protected area in Sicily. Within the park there are different zones - from those that are highly protected to those in which traditional land farming is still present. This area is under protection because of its unique scenery, preserved traditional way of life and use of natural resources and important plant species. The Park is home to 20 municipalities and 250,000 inhabitants who live in this territory (96). The Park is managed jointly by the *Italian Federation* of *Parks* and Nature Reserves and the Regional Park of Sicily Administration. Institutional bodies are represented by the President and the Council of the Park and they together make decisions. The Regional Land and Environment Association was approved by the scientific and technical committee which is concerned about the state of the environmental and gives advice on matters relating to the value and development of the protected area (57).

11. Serbia

Despite an acknowledgment of the need for local community participation and cooperation, Serbia have a long history of a centralised approach to the planning and management of protected areas. In Serbia, in particular, national park planning and management has typically been characterised by a top-down approach (49). In context of participatory processes in managing protected areas Serbia has some good examples of local community involvement in the process of decision-making within protected areas. One such example is Special Nature Reserve "Gornje Podunavlje", where the Management of the protected area meets once a year with the Association of fishermen and they jointly agree on future plans. In the Military Administration "Karadjordjevo" local communities are actively involved in the promotion of its protected natural resources by promoting hunting, fishing and bird watching tourism, etc. (43).

In order to determine the status of protected areas in the territory of Serbia, the RAPPAM workshop was held in Belgrade in February 2009. It was attended by the representatives of three national parks (Kopaonik, Tara, Fruška Gora) and 13 managers of other natural resources. The methodology used for this quick assessment of the state they are in had been adjusted to Serbia and the questionnaire consisted of 100 questions. Based on the questionnaire, certain conclusions were drawn and basic threats and pressures were defined which helped to propose specific measures and methods for the better management and maintenance of natural resources (43). Forest management is listed as one of the problems that occurs in most protected areas. This problem occurs because of illegal logging, exploitation of forest products, but also due to private forests that are part of the protected natural resources, and the managers do not have control over them because there is no communication between the manager and the owner. In addition to this, other problems were mentioned related to water management, which is considered to be the biggest problem in the future, unresolved property and legal relations, changes in land use, tourism and recreation (43).

CONCLUSION

The traditional approaches to protected areas management are currently being challenged. Indeed, protected areas are undergoing a shift from a preservationist paradigm towards an integrated approach. This process is reflective of social changes. One of these social changes is an increasing recognition that local people must be actively involved in conservation and that their needs and aspirations have to be considered, if biodiversity is to be conserved (49). Thus, these social changes increased interest in, and demand for, participation in decision-making processes. New policies have emerged, seeking to promote public participation in planning, decision-making and the management of protected areas.

The examples that are presented in this paper describe various categories of protected areas, which, therefore, have various modes of protection. Each of these cases is from a different political and social context which also has an impact on the management, and it is difficult to compare certain examples. The only comparable issue is the issue of participation/ involvement of local communities in the management, which is present in almost all cases. Some examples from the world show that the management of some protected areas in the past was either not good or the local population was completely excluded from the process of management. The initiative of the local population or the local government improved the management status, and today the participation of local people is mainly active (functional or interactive). According to PIMBERT AND PRETTY (41), these levels of participation are sufficient in order to achieve effective, efficient and sustainable conservation in protected areas. Unlike the examples from the world, participation of local people in protected areas in Serbia is still mainly passive.

Table 5. Examples of protected natural resources with particular reference to the type of participation of the local people in the management of protected areas

Protected areas - examples	MANAGEMENT	PARTICIPATION	COMMENTS
1. NEPAL	- local community, -management is supervised by the committee	- functional	- bad initial management
2. INDIA	- forests are managed by the local community	- functional	- bad initial management, change in order to obtain benefits
3. AUSTRALIA	- co- management	- functional	- example of good progress in management
4. SOUTH AFRICA	- joint management	- functional	- organization gives the land to the local population
5. VIETNAM	- state	- participation by means of consultations	- adjusting categories
6. UNITED KINGDOM	- local community and park management	- interactive participation	- management agreements
7. ECUADOR	- joint management	- interactive participation	- 3 institutions make decisions by consensus
8. BOLIVIA	- local community	- self – mobilization	- management as a response to requirements of indigenous people
9. CANADA	- co-management	- interactive participation	- management as a response to the requirements of indigenous people
10. ITALY	- joint management	- functional	- each park has its own management
11. SERBIA	- state	- passive / participation by means of providing information	- national parks are managed by public enterprises with minimal participation of the local community

In order to achieve sustainable conservation, state legislators and environmental planners should involve local people in management of protected areas and need to identify and promote social processes that enable local communities to conserve and enhance biodiversity as a part of their livelihood system.

REFERENCES

1. ARCHABALD, K., NAUGHTON-TREVES, L. (2001) Tourism revenue-sharing around national parks in Western Uganda: early efforts to identify and reward local communities. *Environmental Conservation* 28: 135–149.
2. BELTRÁN, J. (2000) *Indigenous and Traditional Peoples and Protected Areas: Principles, Guidelines and Case Studies*. IUCN, Gland, Switzerland and Cambridge, UK.
3. BORRINI-FEYERABAND, G. (1996) *Collaborative Management of Protected Areas: Tailoring the Approach to the Context. Issues in Social Policy*. IUCN, Gland, Switzerland.
4. BORRINI-FEYERABEND, G. (2002) Indigenous and local communities and protected areas: rethinking the relationship. In: *Parks, Vol.12, No 2, Local Communities and Protected Area.* Protected Areas Programme, IUCN, Gland, Switzerland. pp. 5-15.
5. Borrini-Feyerabend, G., Kothari, A., Oviedo, G. (2004) Indigenous and Local Communities and Protected Areas: Towards Equity and Enhanced Conservation. IUCN, Gland, Switzerland and Cambridge, UK.
6. BRÜGGERMANN, J. (1997) National parks and protected area management in Costa Rica and Germany: a comparative analysis. In: GHIMIRE, K.B & PIMBERT, M.P. (eds.) *Social Change and Conservation*: *Environmental Politics and Impacts of National Parks and Protected areas*. UNRISD and Earthscan, London, pp.71-96.
7. CAMPBELL, B., MANDONDO A., NEMARUNDWE, N., SITHOLE, B., DEJONG, W., LUCKERT, M., MATOSE F. (2001) Challenges to proponents of common property resource systems: despairing voice from the social forests of Zimbabwe. *World Development* 29: 589–600.
8. Deguignet M., Juffe-Bignoli D., Harrison J., MacSharry B., Burgess N., Kingston N., (2014) 2014 United Nations List of Protected Areas. UNEP-WCMC: Cambridge, UK.
9. DFID (1999) *Sustainable Guidance Sheets: Framework*. DFID, London.
10. DIXON, J.A., SHERMAN, P.B. (1990) *Economics of Protected Areas: A new look at Benefits and Cost.* East-West Center, Earthscan Publications Ltd, London.
11. Eagles, P.F.J., McCool, S.F., Haynes, C.D. (2002) *Sustainable Tourism in Protected Areas, Guidelines for Planning and Management.* IUCN, Gland, Switzerland and Cambridge, UK.
12. FAO (1990) *Participation in Practice, Lessons from the FAO People's Participation Programme.* FAO, Rome.
13. FAO/ECE/ILO JOINT COMMITTEE TEAM OF SPECIALISTS ON PARTICIPATION IN FORESTRY (2000) Public Participation in Forestry in

Europe and North America. ILO, Geneva.

14. FINGER, A., GHIMIRE, K. (1997) Local development and parks in France. In: GHIMIRE, K.B & PIMBERT, M.P. (eds.) *Social Change and Conservation: Environmental Politics and Impacts of National Parks and Protected areas*. UNRISD and Earthscan, London, pp.158-186.
15. FINGER-STICH, A., FINGER, M. (2003) *State versus Participation: Natural Resources Management in Europe*. IIED and IDS, London, UK.
16. GHIMIRE, K. B., PIMBERT, M. P. (1997) Social change and conservation: An overview of issues and concepts. In: GHIMIRE, K. B. & PIMBERT, M. P. (eds.) *Social Change and Conservation: Environmental Politics and Impacts of National Parks and Protected Areas.* UNRISD and Earthscan, London, pp. 1-45.
17. GIBSON, C.C., MARKS, S.A. (1995) Transforming rural hunters into conservationists: an assessment of community-based wildlife management programs in Africa. *World Development* 23 (6): 941-957.
18. GREEN, M. J. B., PAINE, J. (1997) State of the world's protected areas at the end of the twentieth century. Paper presented at IUCN WCPA symposium on "Protected areas in the 21st century: from islands to networks", Albany, Australia, WCMC, Cambridge.
19. GRUMBINE, R. E. (1994) What is Ecosystem Management?. *Conservation Biology* 8 (1): 27-38.
20. Heylings, P., Bravo, M. (2001) "Survival of the fittest? challenges facing the co-management model for the Galapagos Marine Reserve". *CM News* 5: 10–13.
21. HOCKINGS, M., PHILLIPS, A. (1999) How well are we doing? - some thoughts on the effectiveness of protected areas. In: *Parks, Management Effectiveness of Protected Areas*, Vol. 9, No. 2., IUCN, Gland, Switzerland, pp.5-14.
22. IUCN (1993) *Parks for Life: Report of the IVth World Congress on National Parks and Protected Areas*. IUCN, Gland, Switzerland.
23. IUCN (1994) *Guidelines for protected areas management categories*. IUCN, Gland.
24. JACOBSON, S.K. (1995) *Conserving Wildlife: International Education and Communication Approaches*. Columbia University Press, New York, USA.
25. KEMF, E. (1993) *The Law of the Mother: Protecting Indigenous Groups in Protected Areas.* Sierra Club Books, San Francisco.
26. KORTEN, D.C. (1980) Community organization and rural development a learning process approach. *Public Administration Review,* September-October: 480-511.
27. KORTEN, D.C. (1981) The management of social transformation. *Public Administration Review,* November-December: 609-618.
28. KORTEN, D.C. (1990) *Getting to the 21st. Century, Voluntary Action and the Global Agenda*. Kumarian Press, West Hartford.
29. KOTHARI A., SURI, S., SINGH, N. (1997) *Building bridges for conservation–towards joint management of protected areas in India*. Indian Institute of Public Administration, New Delhi.
30. Lockwood, M., Worboys, G., Kothari, A. (eds.) (2006) Managing protected areas, a global guide, IUCN, Earthscan in the UK and USA.

31. MCCRACKEN, J. (1987) Conservation priorities and local communities. In: ANDERSON, D. & GROVE, R. (eds.) *Conservation in Africa- People, Policies and Practice*. Cambridge University Press, Cambridge.
32. MCNEELY, J A (1994) Lessons from the past: forest and biodiversity. *Biodiversity and Conservation* 3 (4): 3-20.
33. MCNEELY, J.A. (1993) *Parks for Life: Report of the IVth World Congress on National Parks and Protected Areas.* IUCN, Gland, Switzerland.
34. MCNEELY, J.A. (1995) How traditional agro-ecosystems can contribute to conserving biodiversity. In: HALLADAY, P. & GILMOUR, D.A (eds.) *Conserving Biodiversity Outside Protected Areas- The role of traditional agro-ecosystem.*The IUCN Forest Conservation Programme, IUCN-The World Conservation Union, Centro de Investigación, F. González-Bernáldez, AMA-Andalucía, pp. 20-40.
35. MCNEELY, J.A. (2001) Roles for Civil Society in Protected Area Management: A Global Perspective on Current Trends in Collaborative Management. In: BUCK, L.E., GEISLER, C.C., SCHELHAS, J. & WOLLENBERG, E. (eds.) *Biological Diversity: Balancing Interests Through Adaptive Collaborative Management.* CRC Press, Boca Raton, FL, pp. 27-49.
36. MEHTA, J.N., HEINEN, J.T. (2001) Does community-based conservation shape favorable attitudes among locals? An empirical study from Nepal. *Environmental Management* 28: 165–177.
37. MURPHREE, M.M. (1993*) Communities as a Resource Management Institution*. International Institute of Environment and Development (IIED) Gatekeeper series No. 36, London, UK.
38. ORLOVE, B. S., BRUSH, S. B. (1996) Anthropology and the conservation of biodiversity. *Annual Review of Anthropology* 25: 329-352.
39. PELUSO, N.L., PADOCH, C. (1996) *Changing Resource Rights in Managed Forests of West Kalimantan, Borneo in Transition: People, Forests, Conservation and Development.* Oxford University Press. Singapore.
40. PHILIPS, A. (1998) *Economic Values of Protected Areas, Guidelines for Protected Area Managers.* IUCN, Gland, Switzerland and Cambridge, UK.
41. PIMBERT, M.P., PRETTY J.N. (1997a) Parks, People and Professionals Putting 'Participation' into Protected Area Management. In: GHIMIRE, K. B. & PIMBERT, M. P. (eds.) *Social Change and Conservation: Environmental Politics and Impacts of National Parks and Protected Areas.* UNRISD and Earthscan, London, pp.297-330.
42. PIMBERT, M.P., PRETTY, J.N. (1997b) Diversity and sustainability in community based conservation, Paper for the UNESCO-IIPA regional workshop on Community-based Conservation, February 9-12, 1997, India, IIED, London, UK.
43. Piščević, N. (2009) Metodologija brze procene i prioritizacija upravljanja zaštićenim područjima (RAPPAM) Ministarstvo zaštite životne sredine i prostornog planiranja Republike Srbije i WWF, Beograd.
44. POFFENBERGER, M., SINGH, C. (1998) Communities and the state: reestablishing the balance in Indian forest policy. In: POFFENBERGER, M. & MCGEAN, B. (eds.)

Village Voices, Forest Choices: Joint Forest Management in India. Oxford University Press, Delhi, India, pp. 56–85.

45. POKHAREL, R.K. (2000) From practice to policy: squatters as forest protectors in Nepal, an experience from Shrijana Forest User Group. *Forests, Trees and People* 42: 31–35.
46. SHANNON, M.A. (2003) Mechanisms for coordination. In: DUBÉ, Y.C. & SCHMITHÜSEN, F. (eds.) *Cross-Sectoral Policy Impacts Between Forestry and Other Sectors.* FAO Forestry Paper 142. FAO, Rome, pp.145-159.
47. SHYAMSUNDAR, P., KRAMER, R.A. (1996) Tropical forest protection: an empirical analysis of the costs borne by local people. *Journal of Environmental Economics and Management* 31: 129–144.
48. Stolton, S., Thi Dao N., Dudley N., (2004) Categorising protected areas in Vietnam, Protected Areas Programme, Vol 14 No 3 Protected Area Categories: 23 – 27.
49. Tomićević, J. (2005) *Towards Participatory Management: Linking People, Resources and Management*. A Socio-Economic Study of Tara National Park. Culterra, Schriftenreihe des Instituts für Landespflege der Albert-Ludwigs-Universität Freiburg, Heft 43, p.186.
50. UNESCO (2000) *Solving the Puzzle: The Ecosystem Approach and Biosphere Reserves.* UNESCO, Paris.
51. Varalakshmi, V. (1998). "Joint Forest Management: Towards a new system of sustainable forestry." *TERI Newswire* IV (7).
52. WALPOLE, M.J., GOODWIN, H. J. (2001) Local attitudes towards conservation and tourism around Komodo National Park, Indonesia. *Environmental Conservation* 28 (2): 160-166.
53. WARNER, K. (1995) Marketing, valuation and pricing of NWFPs. In: DURST, P.B. & BISHOP, A. (eds.) *Beyond Timber: Social, Economic and Cultural Dimensions of Non-Wood Forest Products in Asia and the Pacific*. Proceedings of a regional expert consultation, 28 November–2 December 1994, FAO. Bangkok.
54. WARNER, K. (2003) Moving forward: developing pathways for sustainable livelihoods through forestry. Second international workshop on participatory forestry in Africa Defining the way forward: sustainable livelihoods and sustainable forest management through participatory forestry 18-22 February 2002 Arusha, United Republic of Tanzania, FAO, Rome, pp. 23-30.
55. WELLS, M. P., BRANDON, K. B. (1993) The principle and practice of buffer zones and local participation in biodiversity conservation. *Ambio* 22 (2):157-162.
56. WESTERN, D., WRIGHT, R.M., STRUM, S.C. (1994) *Natural Connections: Perspectives in Community-based Conservation.* Island Press, Washington, DC, USA.
57. http://www.parks.it accessed April 2012

AN OVERVIEW OF THE *Macrocrustacea (Invertebrates-Arthropoda)* IN SPECIAL NATURE RESERVE ZASAVICA

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ABSTRACT

For the past eighteen years of research Fauna Reserve Zasavica total recorded 20 species Macrocrustacea. Subclass Branchiura the reserve is represented with Fam: *Argulidae* and ichtyophagic parasitic species *Argulus foliaceus,* from the subclass Malacostraca, ordo Isopoda present cosmopolitan species *Asellus aquaticus* In the reserve was discovered five of Amphipods, of which three are surface modes (*Dikerogammarus fluviatilis*; *Gammarus balcanicus* and *Gammarus fossarum*), and one semi-underground type (*Synurella ambulans),* underground type *Niphargus valachicus*. Of these Amphipoda *Niphargus valachicus* is a strictly protected species in Serbia. Total discovered three types branhipods and they are: *Chirocephalus brevipalpis*, *Lepidurus apus* and *Cyzicus tetrracerus*. *Chirocephalus brevipalpis* is a rare species, known only from a few localities in Romania and in two areas in Serbia, a report on Zasavica is the westernmost of this kind and the only one south of the Sava and Danube rivers. The species *Lepidurus apus* with very limited distribution in Serbia, found only in two locations in central Banat. Finding kind in Batar tributary is unique because the individuals were found in running water. The Reserve has so far found nine species of ostracods and they are: *Candona aff. candida*, *Cypria ophthalmica*, *Cyclocpris laevis*, *Cyclocypris ovum*, *Eucypris virens*, *Bradleystrandesia reticulata*, *Heterocypris incongruens*, *Cypris puber* and *Ilyocypris sp*. Although widespread and common species in the Euro-Asian continent, with exceptional tolerance to different habitat conditions record of *Candona aff. candida* in Zasavica is the first in Serbia. From the ordo Decapoda and Fam.Astacidae the Zasavici was found *Astacus leptodactylus*, that was submitted to Central Europe in the nineteenth century from the Caspian Sea region and can grow up to 30 cm in length. Type *Astacus leptodactilus* favors relatively calm waters (lakes, ponds, marshes and canals) and is located on the IUCN Red List.

Key words: macrocrustacea, Zasavica.

INTRODUCTION

Reserve Zasavica is located on the border of the two in terms of diversity of crustaceans very important areas of the Balkan Peninsula, which is characterized by extremely rich and unique fauna crab with 783 species of which 203 species are endemic to the area and the Pannonian Plain, which is an important center of diversity branchiopods crab (Karan,T.Petrov,B.,2000). The first information about the flora and fauna of North Mačve and therefore the area of today's Special Nature Reserve Zasavica give Taube,V.F,(1776),Pančić,J.,(1867) and brothers Dombrowski, (1895). There was a period of over half a century of sporadic research by small groups and individual researchers. In 1995. an initiative was launched to protect Zasavice and Decree on previous protection (Official Gazette of RS, 51/95). At the suggestion of the Institute for Nature Conservation of Serbia Government Declares 1997. Special Nature Reserve "Zasavica (Official Gazette of RS, 19/97). This paper aims to show the overall diversity of fauna macro crustacea in SNR Zasavica.

MATERIAL AND METHODS

Material for this study was collected from previously published papers and submitted the report with research in the period from 1997. to 2015. with additional data which is not yet published.

RESULTS AND DISCUSSION

For the past eighteen years of research fauna reserve Zasavica total recorded 20 species Macrocrustacea.

A systematic review of recorded species:

Phyllum: Arthropoda

Podclasses: Branchiura
Fam:*Argulidae*
Species: *Argulus foliaceus* (Linnaeus,1758)

Podclasses: *Malacostraca*
Ordo: *Isopoda*
Species:*Asellus aquaticus* (Linnaeus,1758)

Ordo: Amfipoda
Genus: *Dikerogammarus*
Species:*Dikerogammarus fluviatilis* Mart,1919;

Genus: *Gammarus*
Species: 1.*Gammarus balcanicus* Schaf.,1922
2.*Gammarus fossarum* Koch,1836)
Genus: *Synurella*
Species: 1. *Synurella ambulans* (F.Muller,1846)

Genus: *Niphargus*
Species: 1. *Niphargus valachicus* Dobr. & Man.,1933)

Ordo: Branhipoda
Species: 1.*Chirocephalus brevipalpis* (Orhgidan,1953),
2.*Lepidurus apus* (Linnaeus,1758)
3.*Cyzicus tetrracerus* (Krynicki,1830).

Phyllum: Arthropoda
Classes: Ostracoda
Genus: *Candona*
Species: 1. *Candona aff. candida* (O.F.Muller,1776)

Genus: *Cypria*
Species: 1. *Cypria ophtalmica* (Jurine,1820)

Genus: *Cyclocypris*
Species: 1.*Cyclocypris laevis* (O.F.Muller,1776)
2.*Cyclocypris ovum* (Jurine,1820)
Genus: *Eucypris*
Species: 1.*Eucypris virens* (Jurine,1820)

Genus: *Bradleystrandesia*
Species: 1.*Bradleystrandesia reticulata* (Zaddach,1844)

Genus: *Heterocypris*
Species: 1. *Heterocypris incongruens* (Ramdorh, 1808)

Genus: *Cypris*
Species: 1. *Cypris pubera* O.F.Muller,1776

Genus: *Ilyocypris*
Species: *Ilyocypris sp.*

Ordo: Decapoda
Fam.Astacidae
Species: 1. *Astacus leptodactylus* Eschscholtz,1823,

Subclass Branchiura the reserve is represented with Fam: Argulidae and ichtyophagic parasitic species *Argulus foliaceus* (Linnaeus,1758) (Harry,G.,Born,L.,1981). For this type these are the first published data on reserve.

From the order of Isopoda subclass Malacostraca of the reserve there is a freshwater species of isopods *Asellus aquaticus* (Linnaeus,1758). Freshwater organisms are ancient Isopoda originating from Paleosoic Wilson,(1999). According to George,D.F.W.,(2008) this is a European and cosmopolitan eurivalent species and is present in the whole area of the Reserve both in the trough Zasavice and ephemeral in the surrounding waters.

On the reservation is detected a total of five types of amfipods, three of which are surface species (*Dikerogammarus fluviatilis* March 1919; *Gammarus balcanicus* Schaf.1922 and *Gammarus fossarum* Koch, 1836), and one a semi-underground (*Synurella ambulans* (F.Muller 1846) and one underground type *Niphargus valachicus* well. & Man.,1933) (Karaman,G.,2007). Of these Amphipods *Niphargus valachicus* is a strictly protected species in Serbia, according type is on the IUCN Red List status VU B1 + 2 BCDE (Savić,A.,2007).

Totally there are three types of branhipods and they are: *Chirocephalus brevipalpis* (Orhgidan,1953), *Lepidurus apus* (Linnaeus, 1758) and *Cyzicus tetrracerus* (Krynicki, 1830).

Chirocephalus brevipalpis is a rare species, known only from a few localities in Romania and in two areas in Serbia, a report on Zasavici is the westernmost of this kind and the only one south of the Sava and Danube rivers. *Ch.brevipalpis* early spring lowland species was found from late February to mid-May. It inhabits ephemeral shallow water, with or without vegetation and floodplain forests (Petrov. et.al.,2007). Within the reserve is found at several sites and the site where it regularly every year there is pasture Valjevac.

Lepidurus apus is a type with a very restricted distribution in Serbia, found only on two locations in the central Banatu (Petrov,B.,Petrov,I.,1997). It inhabits clear water with submerged vegetation or the floodplain forests. This is early spring species and is located between February and April (Petrov,B.,Cvetković,D.,(1997). Finding kind in Batar tributary is unique because the specimens were found in running water (Petrov et.al.,2007). Overall *L.apus* western part is present in the reserve, where it is found both in the flooded lane along Batar tributary and the ephemeral wather Jovaca. In contrast to the other sites in, where the company found exclusively females, here at all three activities in their habitat are found bisexual population Petrov, B.,(2012).

Cyzicus tetrracerus is quite common species in Srem (Petrov,B.,Petrov,I.,(1997), which inhabits the ephemeral water of different types. The populations of these spring-summer species is rare. In the reserve this kind was found only once, in Jovaca pond.

The Reserve has so far found nine species of ostracods and they are: *Candona aff. candida* (OF.Muller,1776), *Cypria ophtalmic* (Jurine,1820), *Cyclocpris laevis* (Müller,1776), *Cyclocypris ovum* (Jurine 1820), *Eucypris virens* (Jurine 1820), *Bradleystrandesia reticulata* (Zaddach 1844), *Heterocypris incongruens* (Ramdorh 1808), *Cypris puber* Müller,1776, and *Ilyocypris sp*. Although widespread and common species of the Euro Asian continent and a remarkable tolerance towards different habitat conditions finding of *Candona aff. candida* in Zasavica is the first in Serbia (Petrov et.al.,2007). In central Europe type *Candona aff. candida* occurs in spring (March-April) and is rapidly evolving. Hartmann and Hiller (1977) is considered a permanent form in waters whose temperature does not exceed 18 ^{o}C during the summer. Ostracods are mainly located in the reserve ephemeral water meadows or stick-in-the-mud fields, and are drought resistant eggs. They have mixed copulation and parthenogenetic reproduction and newborn individuals, the ability to immediately swam. These biological attributes allow them to more efficiently survive in these habitats (Horne,D.J.,Cohen,M.,1998). Among the stated ostracodes most common species in the reserve is *Cypris puber* (Petrov et.al.,2007). Zasavica closest sites where these are found in the ostracodes Srem (Karanović,1996). Found in the genus ostracodes *Ilyocypris* and *Cyclocpris* and the reservation by belong to the fauna of the oldest early Holocene (Menković,et.al.,2004).

From the order Decapoda and Fam.*Astacidae* the Zasavici was found *Astacus leptodactylus* Eschscholtz,1823 at two sites (Batar GPS coordinate. 44° 57.694' N, 19° 33,085' E and watercourse Zasavici at Ban's Fields) (Simić, et.al.,2008). Which is inserted in central Europe in the nineteenth century Caspian see and can grow up to 30 cm in length. Type *Astacus leptodactilus* favors the relatively calm waters (lakes, ponds, marshes and channels) and is on the IUCN Red List (Gherardi, F., Souty-Grosset, C.,2010).

A complete overview of the types of sites where they were found is given in Table 1.

How Zasavica watercourse through the Constitution Modran in Mačvanska Mitrovica related to the Sava River, it is interesting to compare the presence of identified species Macrocrustacea the two watercourses.

According to the authors Petrovic,A.,(2014), which deals with a database called 'Biodiversity in aquatic ecosystems in Serbia, ex situ conservation, BASE ex situ.' 'This database contains information on the findings of macroinvertebrates in aquatic ecosystems in Serbia and to between first bibliographic data 1873. to 2012. According to the author of the Sava river is present isopod *Asellus aquaticus* and amphipods *Gammarus fossarum* and *Gammarus balcanicus* which has a Zasavici in two types *Argulus foliaceus* and *Astacus leptodactylus* stated in the Zasavici to the same database were not found in the Sava river.

As part of the regional project " The Sava River " which included research in aquatic macroinvertebrats fauna of the river Sava from Slovenia (peaks) to Belgrade (mouth of the Danube), between 2011. and 2012. The results of this project showed that the Savi present *Astacus leptodactylus* which is noted in the Zasavici (Lucic,et.al.,2015).

Table 1. Complete overview of the types of sites

Species	**Locality**	**Biotops**	**Localitys:**
Argulus foliaceus	2a	O	1. Valjevac pasture 2. Valjevac the forest 2a. Valjevac watercourse 3. Batar 4. Jovača 5. Sadžak 6. Prekopac 7. Neškovine 8. Zovik 9. Vrbovac 10. Modran (Bogaz) 11. Šumareva ćup 12. Ljubinkovića ćup 13. Pačija bara 14. Paljevine 15. Simića ćup 16. Trebljevine 17. Preseka 18. Gajića ćup symbols: + - ephemeral water O - Zasavica watercourse
Asellus aquaticus	Present in the whole area of the Reserve	O, +	
Dikerogammarus fluviatilis	10	O	
Gammarus balcanicus	16	O	
Gammarus fossarum	16	O	
Synurella ambulans	3,4,10, 11, 12,13,14,15,16, 17	O, +	
Niphargus valachicus	1,4,5,6,11,12,13,16,15,17,18	O, +	
Chirocephalus brevipalpis	1,2,4,5,6,8,9	+	
Lepidurus apus	3,4,7	O, +	
Cyzicus tetrracerus	4	+	
Candona aff. candida	3	O	
Cypria ophtalmica	3	+	
Cyclocypris laevis	3,5	+	
Cyclocypris ovum	3	O	
Eucypris virens	1	+	
Bradleystrandesia reticulata	1	+	
Heterocypris incongruens	1,3	O, +	
Cypris pubera	1,4,5	+	
Ilyocypris sp.	3	O	
Astacus leptodactylus	3,16	O	

CONCLUSION

The fauna of the reserve Zasavica total recorded 20 species Macrocrustacea. For ichtyophagic parasitic species *Argulus foliaceus* this is the first published data. There is also a cosmopolitan species *Asellus aquaticus*. A total of five types Amphipod, of which there are three types of surface and one underground and semi-underground type. From Amphipods *Niphargus valachicus* is a strictly protected species in Serbia and is on the IUCN Red List status VU. Of the three types branhipods *Chirocephalus brevipalpis* is a rare species, whose report on Zasavici is the westernmost of this kind and the only one south of the Sava and Danube rivers. Finding kind *Lepidurus apus* in Batar tributary is unique because the specimens were found in running water. The Reserve has so far found nine species of ostracod a record of *Candona aff. candida* in Zasavica is the first data in Serbia. From the order of the Decapoda Zasavici was found *Astacus leptodactylus* which is on the IUCN Red List.

REFERENCES

1. Annonimus (1995) Official Gazette RS, 51/95 Rešenje o prethodnoj zaštiti prirodnog dobra Zasavica
2. Annonimus (1997) Official Gazette RS, 19/97 Rešenje o zaštiti prirodnog dobra Zasavica
3. Dombrowski,E.(1895):Osnovi ornitologije sjeverozapadne Srbije, Glasnik Zemaljskog muzeja,Sarajevo,
4. Douda,K.,Vrtílek,M.,Slavík,O.,Reichard,M.,(2012):The role of host specificity in explaining the invasion success of the freshwater mussel *Anodonta woodiana* in Europe,Biological Invasions 14
5. George,D.F.W.,(2008): Global diversity of Isopod Crustaceans (Crustacea; Isopoda) in freshwater, Hydrobiologia,Springer
6. Gherardi,F., Souty-Grosset,C., (2010): "Astacus leptodactylus". IUCN Red List of Threatened Species. Version 3.1. International Union for Conservation of Nature.
7. Harry,G.,Born,L.(1981):Fauna Evrope, priručnik za raspoznavanje životinjskih vrsta, Mladinska knjiga, Ljubljana
8. Hartmann,Hiller.,(1977): Beitrag zur Kenntnis der Ostracoden fauna des Harzes und seinesnördlichen, Vorlandes (unter besonderer Berücksichtigung des Männchens von Candona candona), 125.Jahre Naturwissenschaftlicher Verein Goslar
9. Horne, D. J.,Koen,M.,(1998): "An assessment of the importance of resting eggs for the evolutionary success of non-marine Ostracoda (Crustacea)". In Brendonck, L.; De Meester, L.; Hairston, N. Title Evolutionary and ecological aspects of crustacean diapause. **52**. Advances in Limnology.
10. Karaman,S.G.,(2007):Amfipoda (Crustacea, Amphipoda) Specijalnog rezervata prirode Zasavica (Srbija), (247.Prilog poznavanju Amphipoda) Zbornik radova Naučno-stručnog skupa Zasavica 2007 sa međunarodnim učešćem, Sremska Mitrovica
11. Karan,T.Petrov,B.,(2000). A Review of the investigations, preliminary-lis of species and diversiti estimation of freshwater and terrestrial crustaceans of the Balkans and FR Yugoslavia, I part, Ekologija,Vol.35, No.I
12. Karanović,I.,(1996): Fauna ostrakoda (Ostracoda, Crustacea) Fruške gore (Vojvodina, Jugoslavija), Magistarska teza, Novi Sad

13. Lucić,A.,Paunović,M.,Tomović,J.,Kovačević,S.,Zorić,K.,Simić,V.,Atanacković ,A.,Marković,V.,Kračun-Kolarević,M.,Hudina,S.,Lajtner,J.,Gottstein,S.,Milošević,Đ.,Anđus,S.,Žganes, K.,Jaklič,M., Simčič,T.,Vilenica,M.,(2015): Aquatic Macroinvertebrates of the Sava River in Milačić,R.,Ščančar,J.,Paunovič.M.,(2015): The Sava River The Handbook of Enviromental Chemistry, Vol.31, Springer
14. Menković,Lj.,Krstić,N.,Nenadić,D.,(2004): Substrukturna depresija zapadnog Srema, Abstrakt 1.Savjetovanja geologa BiH s međunarodnim sudjelovanjem, Banovići
15. Pančić, J. (1867): Ptice u Srbiji. Državna štamparija, Beograd.
16. Petrov,B.,(2012). Preliminarni rezultati istraživanja morfoloških i ekoloških karakteristika vrste Lepidurus apus (Linneaeus,1758) (Crustacea,Branchiopoda,Notostraca) na području Specijalnog rezervata prirode Zasavica, Zbornik naučno-stručnog skupa "Zasavica 2012", Sremska Mitrovica
17. Petrov,B.,Cvetković,D.,(1997): Communiti structure of Brachiopods (Anostraca, Notostraca and Conchostraca) in the Banat province in Yugoslavia, Hydrobiologia
18. Petrov,B.,Miličić,D.,Karan-Žnidaršič,T.,(2007): Brachiopodni i ostrakodni rakovi Specijalnog rezervata prirode Zasavica, Zbornik radova Naučno-stručnog skupa Zasavica 2007 sa međunarodnim učešćem,Sremska Mitrovica
19. Petrov,B.,Petrov,I.,(1997): The status of Anostraca, Notostraca and Conchostraca in Yugoslavia, Hydrobiologia
20. Petrović,A.,(2014): Mogućnost korišćenja baze podataka u strategiji konzervacije biodiverziteta makrobeskičmenjaka kopnenih voda na nacionalnom novou (doktorska disertacija), Univerzitet u Kragujevcu, Prirodno-Matematički fakultet, Kragujevac,
21. Savić,A.,(2007): Slatkovodni beskičmenjaci Balkanskog poluostrva u međunarodnim listama ugroženih vrsta, 9 th.Sympozium on Flora of Southeastera Serbia and Neighbouring Regions, Niš.
22. Simić,V.,Petrović,A.,Rajković,M.,Paunović,M.,(2008): Crayfish of Serbia and Montenegro-The population status and the level of endangerment, Crustaceana 81 (10), Koninklijke Brill NV, Leiden
23. Stevanović & Šinžar-Sekulić (2009).
24. Taube,W.F,(1776): Historische und geografische Beschreibung des königreiches Slavonien und das Herzogthumes Syrmien,Leipzig
25. Wilson,G.D.F., (1999) Some of the deep-sea fauna is ancient, Crustaceana (Leiden) 72

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COMBINATIONAL DORMANCY AND STORAGE BEHAVIOUR OF ENDEMIC *Hypericum adenotrichum* SEEDS IN RELATION TO *ex situ* CONSERVATION

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ABSTRACT

Seed germination strategies of endemic *Hypericum adenotrichum* were studied. The effects of dry storage and cold stratification for12 months, scarification by H_2SO_4 and hormone (250, 500, 1000 ppm GA_3 at three different temperatures (15/10, 20/10 and 25/15°C) and two light conditions (photoperiod, dark) on seed germination of *H. adenotrichum* were examined.

Seeds have combinational dormancy; originated from hard seed coat with physiological dormancy. GA_3 without any other treatment was not successful enough to break the dormancy. Scarification by sulphuric acid and 250 ppm GA_3 combination is the most effective way for germination of *H. adenotrichum* seeds.

Key words: Germination, dormancy, GA_3, stratification, *Hypericum adenotrcihum.*

INTRODUCTION

Hypericum is an important genus for its pharmacological properties and distributed at mild and subtropical regions and Turkey has 89 *Hypericum* taxa and 43 of them is endemic [1]. *Hypericum adenotrichum* is an endemic species which have ethnobotanical, medicinal and economic properties [2, 3]. Because of those properties its germination and conservation procedures are also important [4].

Seed dormancy is a complicated feature of plants that aids in the avoidance of severe climate conditions; and many seeds are dormant at maturity [5].The surrounding tissues can act as a mechanical barrier or chemical germination inhibitors prevent germination [6].Mechanical constraints must be overcome by embryo growth potential [7].Scarification and GA_3 (Gibberellic acid) can help to overcome this process [8].

Seed germination studies can show how the species adapted to its habitat conditions and how it's regulated by environmental conditions [9] and how the seed development is influenced by a particular habitat [10].

Hypericum adenotrichum is distributed at west Anatolia; Ulu Mount (Bursa), between Dursunbey-Alaçam (Balıkesir), Kütahya, Uşak, Erciyes Mount (Kayseri), Aydın Mount

(Aydın) and baba Mount Denizli) [1].Species diversity in Turkey is decreased under the influence of cultivation, industrialization and urbanization in last 300 years. It's very important to preserve the species for sustainable biological conservation and propagation of threatened or endemic species thorough seeds is a cheap, practical and effective method. In this study it's aimed to determine germination requirement and dormancy mechanisms of *Hypericum adenotrichum* as an endemic plant and its germination properties wasn't studied before.

MATERIAL AND METHODS

Seed germination

Seed germination was conducted in sterile, plastic, 9-cm petri dishes. Seeds were placed on a sterilized filter paper moistened with 4 ml of distilled water or GA_3 solution after surface sterilization.

We tested three different temperature regimes for germination experiments: 20/10 °C, 25/15 °C and 15/10 °C (darkness/photoperiod). Germination was recorded for 70 days, seeds were checked twice a week and the germinated seeds were removed. Five replications of 25 seeds per petri dish were used. Germination percentages and Mean germination times (MGT) were calculated.

Seeds were kept at +4°C in petri dishes after sowing for stratification for 12 months in a fridge. Some others were stored in paper bags at room conditions for 12 months. Both group of seeds were incubated at three different temperature regimes and two light regimes.

For scarification, seeds were immersed in 80 % H_2SO_4 for 10 minutes, then washed in running tap water, sown according to the procedure mentioned above, and incubated as mentioned above. GA_3 was applied in concentrations of 250, 500 and 1000 ppm, and distilled water was used for controls.

Final germination (arcsine transformed) and MGT were analysed by ANOVA. All tests were carried out at a significance level of 0.05 using SPSS ver 22 for Windows.

RESULTS

Effects of dry storage on germination and dormancy

Germination percentage and MGT of dry stored *H. adenotrichum* seeds were presented in Table 1. Without dry storage, neither distilled water controls, nor GA_3 (250, 500 and 1000 ppm) were not resulted in germination and so they were not included in the Tables. Seed germination is not stimulated by GA_3 without dry storage. But germination is higher after dry storage and GA_3 combination. After dry storage, seed germination started without GA_3 but it was still very low as10.6 ± 14.8 per cent, but with 250 ppm GA_3 germination percentages increased the highest levels as 72.6 ± 4.3 (incubated at 20/10 °C darkness).

Seed germination is stimulated at some extent after cold wet stratification (Table 2).Controls without stratification were not germinated and so they were not included in the Table 2. After stratification, the highest germination percentage was found as 18.0 ± 20.8 (20/10ºC, photoperiod incubations).

The effects of acid scarification on germination and MGT were given in Table 1. Without acid scarification neither controls, nor GA_3 (250, 500 and 1000 ppm) were not resulted in germination and not included in the Table 1. The highest germination percentage was found as 14.6 ± 13.7 (15/10 °C, Photoperiod) at acid scarification without GA_3. But GA_3 (1000 ppm) and acid scarification combination was found as 79.00 ± 3.3 per cent (20/10 °C, Photoperiod). Germination was found as more rapid at GA_3 and acid scarification combinations incubated at photoperiod (Table 1).

Table 1. Effects of dry storage, and acid scarification on the germination percentage of H. adenotrichum at different temperatures and GA_3 concentrations (Means ± SE) m. month, MGT. mean germination time

Treatment	**Temperature Series**	**Hormone Series**	**PHOTOPERIOD**		**DARKNESS**	
			Final Germination %	**MGT (days)**	**Final Germination %**	**MGT (days)**
12 m dry storage	15/10°C	Distilled water	10.6 ± 14.8	nd	4.4 ± 9.8	nd
		250 ppm GA3	36.0 ± 9.8	50.3 ± 7.0	42.0 ± 12.2	50.9 ± 2.2
		500 ppm GA3	36.2 ± 13.0	49.7 ± 1.8	33.0 ± 15.1	53.3 ± 5.2
		1000 ppm GA3	31.6 ± 7.4	50.7 ± 8.0	37.2 ± 10.4	54.8 ± 4.1
	20/10°C	Distilled water	4.4 ± 9.8	nd	8.8 ± 12.0	nd
		250 ppm GA3	68.4 ± 7.5	32.7 ± 5.0	72.6 ± 4.3	28.6 ± 3.7
		500 ppm GA3	71.4 ± 3.7	27.6 ± 1.9	71.0 ± 6.6	26.6 ± 4.2
		1000 ppm GA3	42.4 ± 25.4	24.4 ± 15.3	59.8 ± 5.8	25.5 ± 1.1
	25/15°C	Distilled water	0.0 ± 0.0	nd	0.0 ± 0.0	nd
		250 ppm GA3	67.8 ± 4.3	26.4 ± 4.0	67.2 ± 7.1	27.5 ± 4.9
		500 ppm GA3	57.8 ± 11.3	19.2 ± 1.4	61.8 ± 11.9	19.6 ± 2.8
		1000 ppm GA3	33.6 ± 16.8	23.1 ± 0.2	66.0 ± 7.2	20.5 ± 2.7
H_2SO_4	15/10°C	Distilled water	0.0 ± 0.0	nd	0.0 ± 0.0	12.0 ± 26.8
		250 ppm GA_3	69.8 ± 5.4	35.9 ± 5.6	62.6 ± 14.8	32.3 ± 21.1
		500 ppm GA_3	66.8 ± 5.4	35.1 ± 7.1	70.0 ± 13.2	27.6 ± 29.2
		1000 ppm GA_3	60.4 ± 5.8	30.7 ± 5.6	73.4 ± 3.5	26.6 ± 16.0
	20/10 °C	Distilled water	9.2 ± 12.9	nd	07.6 ± 10.4	nd
		250 ppm GA_3	77.4 ± 2.9	18.8 ± 4.7	74.0 ± 7.3	20.8 ± 3.3
		500 ppm GA_3	76.6 ± 3.7	20.2 ± 4.1	73.6 ± 14.9	20.6 ± 8.4
		1000 ppm GA_3	79.0 ± 3.3	16.6 ± 3.3	74.4 ± 12.1	8.8 ± 12.0
	25/15 °C	Distilled water	14.6 ± 13.7	35.2 ± 24.0	10.4 ± 15.0	nd
		250 ppm GA_3	71.0 ± 3.8	13.0 ± 2.5	70.6 ± 4.1	11.7 ± 7.1
		500 ppm GA_3	65.4 ± 11.6	13.8 ± 3.0	67.4 ± 6.6	31.6 ± 5.6
		1000 ppm GA_3	54.2 ± 15.4	13.5 ± 1.6	66.8 ± 4.3	0.0 ± 0.0

Table 2. Effects of stratification on the germination percentage of H. adenotrichum at different temperatures and GA_3 concentrations (Means ± SE) m. month, MGT. mean germination time

Treatment	**Temperature Series**	**PHOTOPERIOD**		**DARKNESS**	
		Final Germination%	**MGT (days)**	**Final Germination %**	**MGT (days)**
12 m Stratification	15/10ºC	13.0 ± 12.3	14.8 ± 22.4	11.4 ± 16.9	4.0 ± 5.4
	20/10ºC	18.0 ± 20.8	18.0 ± 20.8	13.0 ± 12.3	7.2 ± 6.6
	25/15ºC	7.6 ± 10.4	nd	15.4 ± 12.0	2.0 ± 4.4

DISCUSSION

The seeds of *H. adenotrichum* were dormant and not germinated without any treatment. But after a certain period of any treatment they started to germinate, though still at low percentages (Table 1).

The fresh and mature seeds can come out of dormancy if they stored in a dry environment (Baskin & Baskin, 1998). So we firstly tried to determine the effects of the dry storage. Seeds are not stimulated to germinate by GA_3 alone without dry storage (Table 1). The highest germination was found after dry storage without GA_3 application as10.6 per cent (15/10 ºC photoperiod). Pérez-García *et al.* (2006) [11] also found significantly higher germination after 15 months of dry storage than 3 months of dry storage in *Hypericum perforatum*. However, seed germination was higher at GA_3 and dry storage combinations reaching to 72.6 per cent after dry storage + 250 ppm GA_3 application (20/10 ºC darkness). Similar results were also found with *H. scabrum* [12] and *H. perforatum* [13] when treated with GA_3.

The light requirement is an important factor for some species. *Hypericum* species generally have light requirement for germination and also have generally low seed germination rates [14; 11; 15; 4; 16]. But, we didn't find any light requirement for *H. adenotrichum*. This feature could permit *H. adenotrichum* seeds to germinate under snow cover or rocky crevices.

We tested germination at three different temperature regimes and found that 20/10 ºC gave better results than 25/15 ºC or 15/10 ºC (Tables 1, 2). In several studies with *Hypericum* species such as *H. philonotis* [4], *H. elodes* [16], *H. perforatum* (Pérez-García *et al.* 2006) suggested that germination was higher at alternating temperatures. The temperature requirements and time for germination widens after cold stratification, this feature is accepted as species specific [17].

Cold and wet stratification is accepted as one of the effective methods for breaking the dormancy [5]; it also helps for a seedling that not to damage by cold temperatures in winter [18]. Seed germination is increased to some extent by cold wet stratification in *H. adenotrichum* seeds (Table 2). *H. philonotis* was suggested to have a complex dormancy and stratification for 0 to 4 weeks resulted higher germination after washing with water [4]. Carta *et al.* (2016) [16] found a significant relationship of cold stratification with alternating incubation temperatures in five populations of *H. elodes*. Seed coat structure is accepted as an important factor for dormancy in alpine plants (19; 20).The mechanical operations such as sand paper or chemical agents such as sulphuric acid can enable water permeability [21]. The hard seed coat also could be a blockage on the physiologically mature seed germination [22] of the *Hypericum* species. The acid scarification and GA_3 combinations were resulted in similar results for other *Hypericum* species; 50 percent for *H. orientale* and 30 percent for *H. pruinatum* [13]. Gibberellins were suggested to increase embryonic growth potential and reduce the constraint of the covering layers of the seed coat (22; 7].

CONCLUSIONS

Under view of our observations we suggest *H. adenotrichum* seeds have combinational dormancy (PY+PD). We suggest sulphuric acid scarification and 250 ppm GA_3 combination for improve germination of *H. adenotrichum* seeds. *H. adenotrichum* is a valuable species for its pharmacological and ecological properties.

REFERENCES

1. Davis P.H. (1967) Flora of Turkey and the East Aegean Islands. Vol. 2. Edinburgh University Press, Edinburgh, UK, 396-397 pp.
2. Baytop T. (1999) *Türkiye'de Bitkiler ile Tedavi, Geçmişte ve Bugün.* Nobel Tıp Kitabevleri, İstanbul.
3. Erken S., Malyer H., Demirci F., Demirci B., Baser K.H.C. (2001) Chemical investigations on some *Hypericum* species growing in Turkey. *I. Chem Nat Compd*, 37, 434–438.
4. Sanchez-Coronado M.E., Olvera C., Marquez-Guzman J., Macias-Rubalcava M.L., Orozco S., Anaya A.L., Orozco-Segovia A. (2015) Complex dormancy in the seeds of *Hypericum philonotis*. *Flora*, 213, 32-39.
5. Baskin C.C., Baskin J.M. (1998) *Seeds: Ecology, biogeography and evolution of dormancy and germination.* Academic Press. San Diego, USA.
6. Bewley J.D., Black M. (1997) *Seeds: Physiology of development and germination*. Plenum Press, New York, USA.
7. [7] Kucera B., Cohn M.A., Leubner-Metzger G. (2005) Plant hormone interactions during seed dormancy release and germination. *Seed Science Research*, 15, 281-307.
8. Pérez-García F. (2008) Effects of cryopreservation, gibberellic acid and mechanical scarification on the seed germination of eight endemic species from the Canary Islands. *Seed Science and Technology,* 36, 237-242.
9. Finch-Savage W.E., Leubner-Metzger G. (2006) Seed dormancy and the control of germination. *New Phytologist*, 171, 501-523.
10. Van Assche J., Van Nerum D., Darius P. (2002) The comparative germination ecology of nine *Rumex* species. *Plant Eco*logy, 159, 131-142.

11. Pérez-García, F., Huertas, M., Mora, E., Peña B., Varela F., González-Benito, M. E. (2006) *Hypericum perforatum* L. seed germination: interpopulation variationand effect of light, temperature, presowing treatments and deed desiccation. *Genetic Resources and Crop Evolution,* 53, 1187-1198.
12. Çırak C., Ayan A.K., Kevseroğlu K. (2006) Physical and physiological seed dormancy of some *Hypericum* species growing in Turkey. *Plant Breeding and Seed Science*, 53, 3-8.
13. Çırak C. 2007. Seed germination protocols for *ex situ* conservation of some *Hypericum* species from Turkey. *American Journal of Plant Physiology*, 2, 287-294.
14. Camas N., Caliskan O. (2011) Breaking of seed dormancy in *Hypericum leptophyllum* Hochst. an endemic Turkish species. *Journal of Medicinal Plants Research*, **5,** 6968-6971.
15. Carta A., Probert R., Puglia G., Peruzzi L., Bedini G. (2016) Local climate explains degree of seed dormancy in *Hypericum elodes* L. (Hypericaceae). *Plant Biology*, 18, 76-82.
16. Jaganathan G. K., Dalrymple S. E., Liu B. (2015) Towards an Understanding of Factors Controlling Seed Bank Composition and Longevity in the Alpine Environment. *Botanical Reviews,* 81, 70–103.
17. Vranckx G., Vandelook F. (2012) A season and gap-detection mechanism regulates seed germination of two temperate forest pioneers. *Plant Biology*, 14, 481-490.
18. Urbanska K.M., Schütz M., (1986) Reproduction by seed in alpine plants and vegetation research above timberline. *Botanica Helvetica*, 96, 43-60.
19. Zuur-Isler D. (1982) Germination behaviour and early life phases of some species from serpentine soils. *Berichte des Geobotanischen Institutes Swiss Federal Institute of Technologu, Stiftung Rübel,* Zürich, 49, 76-107.
20. Abdullah M.M.F., Jones R.A., El-Beltagy A.S. (1989) An efficient method to overcome seed dormancy in Scotch brom (*Cytisus scoparius*). *Environmental and Experimental Botany*, 29, 499-501.
21. Chen S.Y., Shing-Rong K., Ching-Te C. (2008) Roles of gibberellins and abscisic acid in dormancy and germination of red bayberry (*Myrica rubra*) seeds. *Tree Physiology*, 28, 1431-1439.

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THE CONFIRMATION OF *Iris spuria L.* AT „MALI VRSACKI RIT”

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ABSTRACT

During 2016, Iris spuria L. was discovered at “Mali vršacki rit” in the area with the central coordinate at 45° 09’ 31" N, 21° 19’ 09" E. At the same place, plants in flower were observed in previous years, but it wasn't confirmed by experts. The population of the plants is stable but threatened by arson of surrounding agricultural fields. This is rare species in Serbia, especially in Vojvodina province and must be protected from extinction.

Key words: Iris spuria, Mali vršački rit, endangered plant species.

INTRODUCTION

Institute for Nature Protection of Serbia proposed a „Mali vršački rit” for protection as a nature park Category II - a natural resource of great significance, or areas to manage species and habitats (IV Habitat / Species Management Area). Together with the Vršac Mountains, it is within one of the 42 important bird areas (IBA - Important Bird Area) in Serbia. This little swamp is a unique environmental, structural and functional unit and the nutritional base for many species.[1] European alkali grass-Puccinellia distans (Jacq.) Parl., a poor grass-Glyceria declinata Brébiss, steppe lizard-Podarcis taurica (Pallas), a ferruginous duck-Aythya nyroca (Güldenstädt) and a corncrake- Crex crex (Linnaeus) stand out as the endangered species of plants and animals.

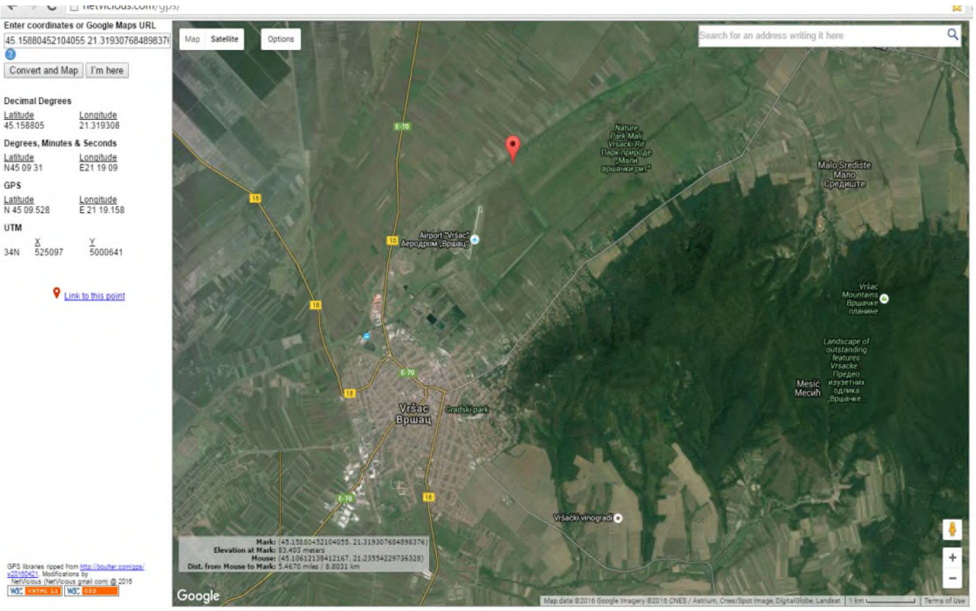
MATERIAL AND METHODS

About 100 Iris spuria plants were found in 2016 on the site of „Mali vršački rit”. They were positioned by GPS and photographed in the field. Zoran Gavrilović was identified them as a species of Iris spuria L. which was confirmed by Jožef Dožai, moderator of taxonomic groups on BioRaS portal informative resource about Serbian wildlife and a sophisticated tool for harvesting field observations of animal, plant and fungus species collected by civil society in Serbia.[2]

RESULTS AND DISCUSSION

Genus Iris contains around 300 species which are widely distributed across the Northern Hemisphere.[3] The species is common from Denmark south to Spain, Algeria east through central Europe to the Caucasus and Iran. The species found in seasonally inundated grassland, swamps, bogs marshes, shrubs, maquis, damp meadows, salty flats and alluvial plains.[4] This is perennial, 30-80 cm tall plant with leaves shorter than a stem, narrow shaped, only 5-10 mm. The stem is bluish-greyish, cylindrical with prominent ribs. The flowers (2-5) are on the short stalks, the external lobes are a purple-blue to dark purple nerves with a yellow ribbon in the middle and they are not bearded hairy. They bloom from May to June. The fruit is a capsule with a long spike with stubby fins.

The field of irises in bloom at the central coordinate at 45° 09' 31" N, 21° 19' 09" E in „Mali Vršački rit", was found in May 2016. After the determination a species as the Iris spuria L., it was confirmed that is a new species at this area.



Enter coordinates or Google Maps URL

45.15880452104055 21.31930768489837

Decimal Degrees
Latitude 45.158805
Longitude 21.319308

Degrees, Minutes & Seconds
Latitude N45 09 31
Longitude E21 19 09

GPS
Latitude N 45 09.528
Longitude E 21 19.158

UTM
34N X 525097 Y 5000641

Mark: (45.15880452104055, 21.319307684898376)
Elevation at Mark: 83.403 meters
Mouse: (45.10612138412167, 21.23554229736328)
Dist. from Mouse to Mark: 5.4670 miles / 8.8031 km

Figure 1. Locality where it is found *Iris spuria L.* compared to "Vrsačke Planine"
(GoogleEarth®)

Enter coordinates or Google Maps URL
45.15880452104055 21.3193076848983

Decimal Degrees

Latitude	Longitude
45.158805	21.319308

Degrees, Minutes & Seconds

Latitude	Longitude
N45 09 31	E21 19 09

GPS

Latitude	Longitude
N 45 09.528	E 21 19.158

UTM

	X	Y
34N	525097	5000641

Mark: (45.15880452104055, 21.319307684898376)
Elevation at Mark: 83.403 meters
Mouse: (45.15874021530321, 21.319023370742798)
Dist. from Mouse to Mark: 0.0145 miles / 0.0234 km

Figure 2. The first confirmed records of *Iris spuria L.* at „Mali Vršački rit" on May of 2016 (GoogleEarth®)

Figure 3. The photo of *Iris spuria L.* recorded on May of 2016 (photo:Zoran Gavrilović)

The iris spuria L. is native in Algeria; Austria; Czech Republic; Denmark; France (France (mainland)); Germany; Hungary; Iran, The Islamic Republic of; Russian Federation; Slovakia; Spain (Spain (mainland)); Sweden; Turkey (Turkey-in-Asia) without significant threats, and is considered as Least Concern by IUCN Red List Category and Criteria.[4] But it is a rare plant of the flora in The Republic of Serbia, it was found only in six locations and every new finding is important for the biodiversity of the country.[5]

CONCLUSION

Wetland ecosystems hold an important part of Serbia's biodiversity. Although "Mali Vršački rit" spreads only at 931.20 ha, this is an especially important area for birds, dragonflies, amphibians and the plants depend on wetlands. The new species in the flora of this area is a good sign for biodiversity enhancement which leads to sustainable development. Protection of the biological and landscape diversity of "Mali Vršački rit" will improve benefits for the local people.

REFERENCES

1. Stojnić, N., Habijan-Mikeš, V., Dobretić, V., Delić, J., Pil, N., Kovačev, N., Perić, R., Kovačević, B., Bošnjak, T., Sabadoš, K., Stanišić, J., Banjac, M, Čalakić, D. 2012. Studija zaštite: Zaštićeno stanište "Mali vršački rit", 1-123 . Pokrajinski zavod za zaštitu prirode, Novi Sad.
2. Dožai, J., Mišljenović, T., Ranković, D, Savić, D, Stanković, M. 2017. Moderatori unosa u bazu podataka za biljke. BioRaS. http://bioras.petnica.rs
3. Kaššák, P. 2014.Screening of the chemical content of several Limniris group Irises,11-14. Journal of Pharmacognosy and Phytochemistry 3 (2).
4. Kavak, S. 2014. Iris spuria. The IUCN Red List of Threatened Species 2014:e.T200242A42327335. http://dx.doi.org/10.2305/IUCN.UK.2014-1.RLTS.T200242A42327335.en
5. Vajgand, D. K., Vajgand, LJ. M, Vajgand, K. A. 2003. Iris spuria L. (Iridaceae) AT TWO NEW LOCALITIES IN THE VOJVODINA PROVINCE, , 83—89, Zbornik Matice srpske za prirodne nauke / Proceedings for Natural Sciences, Matica Srpske No. 104, Novi Sad.

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THE EVIDENCE OF CANIS LUPUS AT "VRSAC MONTANTAINS"

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ABSTRACT

The trail "Lovačko imanje-Vršišor" was marked by wolf spoor on 24 December of 2016. Additionally, the photos recorded by the trail camera on 6 and 10 February of 2017, showed the presence of 3 individuals of this species on "Vršac Mountains". In this area until the end of the nineties of the last century, the wolf population was stable in the form of two to three packs. Factors that have contributed to the decrease of the wolf population in this area are the reduced number of the hunting game, the livestock in extensive agriculture, illegal hunting and urbanization.

Key words: Canis lupus, Vršac Mountains, wolf population.

INTRODUCTION

The major food sources for wolves are deer, roe deer, wild boar and smaller mammals, such as rabbits and rodents. In areas with developed extensive stock farming, they feed livestock, especially if it is not well guarded[1]. Wolves live in the whole northern hemisphere and can be found in almost all types of habitats, if it is not persecuted, and there is enough food.

They are protected by the Convention on International Trade in Endangered Species of Wild Fauna and Flora – CITES (Appendix I)[2], the Convention on the Conservation of European Wildlife and Natural Habitats – Bern Convention[3], the Directive on the conservation of natural habitats and of wild fauna and flora, Regulation on Proclamation and Protection of Strictly Protected and protected wild species of plants, animals and fungi - Appendix I – strictly protected species (Official Gazette of the Republic of Serbia, no. 05/10 and 47/2011)[4] and is located on the red list of endangered species by IUCN and the European red list.

MATERIAL AND METHODS

Since 2010, data on the presence and activities of the wolf in the area of protected natural resource „Vršac Mountains" are intensive collects. Their movements and feeding are followed up through footprints and excrements and monitored by trail cameras.

RESULTS AND DISCUSSION

Based on the data collected from 2010 till now, it was concluded that the presence of wolves is the most intensive at the area that borders with Romania (Korkana and Donji Vršišor). On 2008 in Vojvodina, we visited with Tajti Judit two areas: Vršac Mountains (whose highest peak is at 461 meters above sea level, in the territory of 11,000 hectares, there were 15 wolves, which constituted 3 packs) and Deliblato sands where on 35,000 hectares 20 wolves were lived. Three years ago, there were twice as many, but the population has halved because of the serious epidemic of mange (natural selection). This is information acquired from Jovan Bradvarović, who in 1999 wrote a master's thesis of wolves, and who is a long time hunter in this area[5]. Also, the traces were seen on Gudurički peak until Kulmea Mare (ridge above the village Malo Središte). It is interesting that in the locality of a Lisičija glava, at the feeding place for birds of prey is not recorded presence of wolf. This place is monitored by trail cameras since 2008. By the nineties, this position has been the main focus of one of the two alpha couples which are registered in that period. On this territory, the alpha pair changed in the period from 2010 to 2017 but the pack of wolves was not always active. In the meantime, some numbers of wolves ranged more like wandering individuals.

Figure 1. Wolf footprints on 24 December of 2016 (photo: Milivoj Vučanović)

Figure 2. The photos recorded by the trail camera on 6 February of 2017 (photo: Milivoj Vučanović)

The footprints of wolves are registered on the crosscut "Lovačko imanje-Vršišor" on 24. December of 2016. Trail cameras located at the aforesaid position were recorded the presence of wolves on 6 and 10 February of 2017.

Figure 3. The photos recorded by the trail camera on 10 February of 2017 (photo: Milivoj Vučanović)

CONCLUSION

The wolf is one of the animals that are deeply woven into the human psyche and culture. Many of the societies respected a wolf and gave him a mythical character, for the ancient Slavs, for example, the wolf was a sacred animal. Prejudice, damage to livestock, the impact on the hunting game and the lack of communication between stakeholders contributed to the vulnerability of the species which had once a wide range of living habitats. Thanks to the efforts of the custodian of PIO "Vršac's Mountains", PE "Vojvodinašume", which manages forests in this area, as well as NGO-s dealing with the protection of nature, again, this species arrived at their earliest habitat.

Acknowledgment

The authors would like to thank Miroslav Vrekić, forestry engineer, employed in PE "Vojvodinašume", who was intensively involved in the tracking of wolves on Vršac's Mountains and Fodor Tamás a teacher of Hungarian and German language, for the translation of the dissertation of Judit Tajti.

REFERENCES

6. Štrbenac, A., Desnica, S., Kusak, J., Huber, Đ, Jeremić, J., Oković, P., Majić-Skrbinšek, A., Vukšić, I., Katušić, L., Gomerčić, T., Bišćan, A., Zec, D. et Grubešić, M, 2010. Plan upravljanja vukom u Republici Hrvatskoj za razdoblje od 2010. do 2015.,1-128, Republika Hrvatska, Ministarstvo kulture, Zagreb.(in Croatian)
7. CITES et UNEP. 2011. Convention on International Trade in endagered Species of Wild Fauna and Flora, Appendices I, II, III,., 1-42 Council of Europe, France,Strasbourg.
8. CITES et UNEP. 1979. Convention on International Trade in endagered Species of Wild Fauna and Flora,.Bern., 1-10, European Treaty Series - No. 104, Council of Europe, France,Strasbourg.
9. Pravilnik o proglašenju i zaštiti strogo zaštićenih divljih vrsta biljaka, životinja i gljiva, 2010 i 2011, 1-136, Službeni glasnik RS, br. 5/2010 i 47/2011).Beograd. (in Serbian)
10. Tajti, J. A farkas (Canis lupus) védelmi helyzete hazánkban és Erdélyben, 2008.1-65. Nyugat- Magyarországi Egyetem Erdőmérnöki Kar, Vadgazdálkodási és Gerinces Állattani Intézet. Sopron.(in Hungarian)

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A CONTRIBUTION TO THE KNOWLEDGE ON THE DISTRIBUTION OF NATIVE CRAYFISH *Austropotamobius torrentium* (SCHRANK, 1803) IN SERBIA

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ABSTRACT

The native crayfish species *Austropotamobius torrentium* presumably inhabits mountainous streams at higher altitudes. As Serbia is one of few countries in its native range with general lack of data regarding conservation status of *A. torrentium*, there is a need to provide up-to-date basic data regarding distribution and population status of the species. Therefore, as a starting point for planned future investigation in this paper we present a current state of knowledge of *A. torrentium* distribution in the target area. To date based on previously published and new findings, stone crayfish was found at 48 localities, covering seven major river basins, in total.

Key words: stone crayfish, new findings, Serbia.

INTRODUCTION

Stone crayfish *Austropotamobius torrentium* (Schrank, 1803) is one of a five autochthounous decapod species in Europe and one of three recorded in Serbia. It inhabits unpolluted mountainous streams of the Danube and Elbe basins in South-eastern and Central Europe [1]. According to IUCN criteria (Version 3.1) [2] this species is categorized as "Data Deficient" with decreasing population trends in the majority of countries.

Serbia is one of few countries in its native range with general lack of data regarding status of this species. According to the Appendix I of the Book of Regulations on the designation and protection of protected and strictly protected wild species of plants, animals and fungi [3] it is listed as strictly protected species.

Increased anthropogenic pressures on aquatic habitats – pollution, habitat destruction, construction of small hydropower plants, as one of the most frequent hydromorphological alterations with severe impact are the most threatened factors that cause population declines in a majority of countries [4, 5]. Regarding distribution and conservation of this protected species some steps were already undertaken [6, 7, 8, 9] but there is obvious need to fill existing gaps with continued and more detailed investigation. The aim of this paper is to summarize current knowledge of *A. torrentium* distribution in Serbia, as the basis for future investigation.

MATERIAL AND METHODS

The information regarding the distribution of *A. torrentium* presented in this paper were obtained from available literature [7, 9], and unpublished recent data from regular field research conducted by Institute of Biology and Ecology, Faculty of Science, University of Kragujevac and Institute for Biological Research „Siniša Stanković", University of Belgrade. Individuals of the stone crayfish were collected by hand or LiNi traps. These are cylindrical, folding nets with two conical entrances with 15 mm mesh size. In traps bait was placed in order to attract crayfishes, usually small part of smelly meat (hot dog or salami). With a long rope or stones traps were secured and left in a water over night for 10 hours. In total, eight to ten traps were placed in a stream along transect of 100 m. All caught individuals were kept in plastic containers for measurement. Also, leg or antennal tissue were taken and preserved in 95% ethanol for further genetic analysis.

RESULTS AND DISCUSSION

In total *A. torrentium* was recorded at 48 localities in Serbia (Figure 1). Among them, during recent fieldwork at 13 new localities the presence of this crayfish was confirmed. Out of ten major drainages in Serbia, seven of them were inhabited by *A. torrentium* – the Danube, Drina, Kolubara, Zapadna Morava, Južna Morava and Timok basins, as well as drainages of rivers belonging to the Aegean sea basin. The distribution of stone crayfish is restricted presumably to the springs and streams with stony bottom in mountainous parts of the western, southern and eastern Serbia, but according to literature [7] the densest populations were found in watercourses at lower altitude (500 m).

In the same paper authors assessed the population status of the species as good, with adequate sex ration and age structure. As those results were published nearly ten years ago, and having in mind a general decreasing population trend of the species in majority of countries within its range there is need to re-evaluate its status. As the main treats to *A. torrentium* spreading of alien crayfish species, in addition to overall deterioration of water habitats could be singled out. [10]. Also, due to habitat deterioration (canalization of the lower stretches and building of small hydropower plants) natural dispersion of the stone crayfish throughout watercourse is enabled and they are remaining isolated is the headwater section [11].

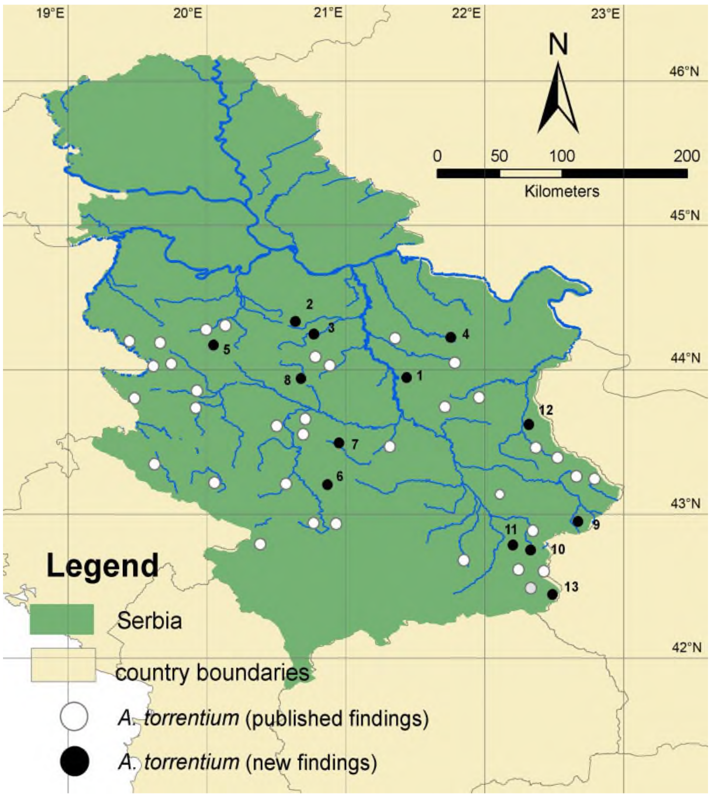

Figure 1. New findings localities codes: 1) Izgara (Sinji Vir), 2) stream Jarmenovački potok, 3) river Javorska reka, 4) river Crna reka (Mlava), 5) river Crna reka (Divčibare), 6) stream Šutanovački potok, 7) river Polonska reka, 8) river Boračka reka, 9) Visočica, 10) river Jelovička reka, 11) river Vučja reka, 12) Belorečka Reservoir, 13) river Brankovačka reka.

Future investigations are planned for next two years. Beside already documented localities, rivers and streams considered to be suitable for inhabiting *A. torrentium* will be studied, at least one stream for each drainage. Eventually presence of the species in the northern part of the country (Fruška Gora and Vršačke planine mountains) will be checked in order to find isolated populations. To describe localities, following data will be used: mean width and depth of the watercourse, bottom type (according to AQEM protocol and standardized crayfish protocol), water temperature, average surface speed of the water, conductivity, pH and coordinates.

Field work will be focused on detailed investigations of recorded populations. For each caught individual symptoms of diseases, injuries and presence of epibionts will be observed. In the same period samples for DNA analyses will be collected. Genetic data will provide basis for estimating population diversity and accompanied with habitat data, will provide better insight into populations status. Found haplotypes will be compared to the already known and will classify them into existing phylogenetic lines.

Important aspect of the investigation will be to determine major threatened factors for survival of *A. torrentium.*

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REFERENCES

1. Kouba, A., Petrusek, A., Kozák, P. 2014. Continental-wide distribution of crayfish species in Europe: update and maps. Knowledge and Management of Aquatic Ecosystems 413: 05.
2. Füreder, L., Gherardi, F., Souty-Grosset, C. 2010. *Austropotamobius torrentium*. The IUCN Red List of Threatened Species 2010: e.T2431A9439449. http://dx.doi.org/10.2305/IUCN.UK.2010.RLTS.T2431A9439449.en
3. Anonymus 2010. Book of Regulations on the designation and protection of protected and strictly protected wild species of plants, animals and fungi, Appendix I. Official Gazette of Republic of Serbia 5/2010 and 47/2011.
4. Füreder, L., Machino, Y. 1998. Historische und rezente Verbreitung von Flusskrebsen in Tirol, Südtirol und Vorarlberg. In: Eder, E., Hödl, W. (Hrsg.) Flusskrebse Österreichs. Stapfia 58: 77-88.
5. Füreder, L., Edsman, L., Holdich, D.M., Kozák, P., Machino, Y., Pöckl, M., Renai, B., Reynolds, J., Schulz, H., Sint, D., Taugbøl, T., Trouilhé M.C. 2006. Indigenous crayfish habitat and threats. p 25-48. In: Souty-Grosset, C., Holdich, D.M., Noel, P.Y., Reynolds, J.D., Haffner, P. (eds) Atlas of Crayfish in Europe, Patrimoines naturels, 64, Muséum national d'Histoire naturelle, Paris, pp. 188.
6. Karaman, M. S. 1961. Slatkovodni rakovi Jugoslavije. Publikacije stručnog udruženja za unapređenje slatkovodnog ribarstva Jugoslavije 3: 1-3. (in Serbian)
7. Simić, V., Petrović, A., Rajković, M., Paunović, M. 2008. Crayfsh of Serbia and Montenegro – the population status and the level of endangerment. Crustaceana 81(10): 1153-1176.
8. Simić, V., Magiure, I., Rajković, M., Petrović, A. 2015. Conservation strategy for the endangered crayfish species of the family Astacidae: the ESHIPPO crayfish model. Hydrobiologia 760(1): 1-13.
9. Petrović, A., Rajković, M., Simić, S., Magiure, I., Simić, V. 2013. Importance of genetic characteristics in the conservation and management of crayfish in Serbia and Montenegro. Bulgarian Journal of Agricultural Science 19(5): 1093-1104.
10. Maguire, I., Jelić, M., Klobučar G. 2011. Update on the distribution of freshwater crayfish in Croatia. Knowledge and Management of Aquatic Ecosystems 401: 31.
11. Maguire, I., Gottstein-Matočec, S. 2004. The distribution pattern of freshwater crayfish in Croatia. Crustaceana 77(1): 25-47.

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DETERMINATION OF THE EMISSIVITY OF COATINGS FOR PREPARATION OF SAMPLES IN THERMOGRAPHIC TESTINGS

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ABSTRACT

In order to increase the product quality and energy efficiency of the cold plastic deformation plant, the numerous laboratory studies of deformation zone on treated materials were being conducted. In order to examine the material flow and stress distribution through deformation zone, in recent times the method of thermography is commonly used. The most significant impact on accuracy of thermographic method has the emissivity of test sample. Therefore, it is of great importance to use the coatings over test samples with known and constant value of emissivity in the investigated temperature range. The paper presents the results of research of the affect of temperature changes, during cold plastic deformation, on the value of emissivity of three selected coatings.

Key words: cold plastic deformation, thermography, emissivity, energy efficiency.

INTRODUCTION

To minimize the impact of pollutants on the environment by reducing energy consumption is increasingly implemented measures aimed at increasing energy efficiency. To minimize the impact of pollutants on the environment by reducing energy consumption, the measures aimed at increasing the energy efficiency are increasingly implemented. Metallurgical production has a significant impact on the environment, particularly in manufacturing processes of metal alloys and their forming into semi-finished and finished products. Today, in the metallurgical industry, in order to reduce energy consumption and environmental pollution are being developed new or improved materials and/or improved technological production processes. In metallurgical production of finished ferrous and nonferrous products, the plastic processing makes the large share of production. A significant part of this production refers to cold plastic deformation to achieve the tight tolerances of the final products, for example, in the production of cold-rolled tubes of carbon, alloyed and stainless steel. With this technology it is possible to achieve the reductions of 75-85% in tube walls and up to 65% of tubes diameter achieving high productivity and high tolerance [1]. Cold plastic deformation implies that there are no mechanisms of recovery and recrystallization. Due to various factors such as the orientation and size of grains, grain boundary mobility, reduction, strain rate, presence of other phases such as precipitates, there is an increase in deformation resistance [2,3]. In order to ensure further deformation, it is necessary to increase the pressure force of tool on rolled piece, which results in specific energy consumption and wear of tool.

Deformation, strengthening and act of tool on the rolled piece result in an increase of temperature of the deformed piece. A part of generated heat transfers is transferred onto the tool, a part is accumulated in rolled piece, and the remaining part is emitted in the environment [4]. The increase in temperature can cause instability in the process of cold deformation, since directly affects the contact friction and metal plasticity. Heating of tools can cause the changes in tool dimensions and thus the variations in dimensions of finished product. Therefore, it is necessary to apply the cooling of tools during the process of cold deformation, using various emulsions, what causes additional power consumption and the subsequent disposal of waste coolant. To increase the energy efficiency of the plant, it is necessary to measure the temperature increase during cold plastic deformation, aiming to rationalize the consumption of coolant and the energy necessary for implementation of the technological process of rolling. Measuring the temperature changes during deformation in a rolling stand is difficult to perform, mainly because of limited access to deformation zone. In order to simulate the conditions during cold rolling, a various laboratory researches have been carried out to investigate the influence of each parameter of the plastic deformation separately. By measuring the temperature change during the plastic deformation in the laboratory conditions, it is possible to determine temperature changes in the conditions of actual production and what parameters and the extent to cause these changes. Optimization of these parameters increases the energy efficiency of the process of plastic deformation in industrial conditions.

THERMOGRAPHIC TESTING OF COATINGS

Accordingly, to determine the temperature increase in the real deformation processes, it is necessary to develop a model that allows the prediction of temperature changes due to changes of the deformation parameters. Measuring the temperature changes during deformation in laboratory conditions may be performed with various measurement methods. The conventional method of measuring the temperature variation is achievable by using a contact thermometer. Method of thermography is a non-contact method for measuring temperature distribution. The method is based on measuring the temperature changes using an infrared camera. Camera measures current temperature of a body by detecting infrared electromagnetic waves in invisible spectrum of light.

If the body is at a temperature below 500°C, all of its heat energy is emitted within the infrared spectrum. The temperatures during the cold plastic deformation are well below that temperature, and therefore it is possible to measure by infrared camera the whole thermal radiation of observed body. In order to achieve the accurate thermographic measurements, it is essential to know the exact value of surface emissivity. By knowing the exact value of the test sample emissivity and adjusting the parameters of thermal camera onto this value, the exact value of temperature can be measured by the infrared camera. Emissivity is a function of material, surface structure, wavelength, direction of emitted radiation and temperature, but primarily depends on the material and surface condition. For most materials the emissivity decreases with increase in temperature. If the value of emissivity of a certain material is unknown, when using the infrared pyrometers and thermal cameras for as accurately as measurement of temperatures, a slightly higher emissivity is usually taken from the one listed in the available tables [5,6]. In this way the accuracy of measurement is improved, but not fully. Therefore, using thermographic methods it is necessary for the laboratory studies of temperature changes to determine the exact value of the surface emissivity. There are various methods for determining the emissivity of body surface. One of them is setting up on the body a label of known emissivity and after that it is necessary to measure the exact value of its temperature. The value of emissivity on the pyrometer must be adjusted until the same temperature reading on the observed surface without the label is reached [5,7]. Another way is to use a device which represents the ideal black body. It is necessary to keep on the same temperature both the device and the body to whom is necessary to identify emissivity. Pyrometer is first set to the ideal black body in order to measure the exact temperature and then the emissivity of the pyrometer must be adjusted until the same value of temperature of the observed body is reached. This method requires an expensive equipment and a larger number of measurements. One of the practical methods, which is included in the ASTM standards as a method of determining the emissivity, is the application of a contact thermometer with high measuring accuracy [8,9]. First it is necessary to measure the temperature of the observed body with a contact thermometer, and then the emissivity of pyrometer or infrared camera must be adjusted until the same temperature value is reached. Since the emissivity of the body can vary over its surface due to impurities on the surface as well as surface roughness, reflection, color, etc., it is necessary to equalize the emissivity of the observed surface by using some of the available methods. The uniform emissivity over the whole body surface may be achieved by applying an adequate coating. Also, depending on the chosen coating it is necessary to measure the change in the value of emissivity with increase in temperature. Using a matte coating, the reflection is removed, and the high accuracy of thermography measurement can be reached. Because the plastic deformation leads to an increase in temperature of deformed body, the question is whether this increase has an impact on the emissivity of coatings for sample preparation. For this reason, the goal of the research was to determine which of the selected coating has a constant emissivity factor in the area of temperature increases that occur during cold plastic deformation in the deformed body.

For non-contact temperature measurement the infrared camera VarioCAM® M82910 producer JENOPTIK was used. The camera has sensitivity of 80 mK at room temperature. Camera was mounted above of the examined samples at distance of 0.8 m. Before measurements the camera was calibrated within the measuring range 0÷300°C by adjusting its parameters on the laboratory conditions: ambient temperature of 16.5°C and humidity of 48%. Samples for testing of coatings were cut from low-carbon steel strip with the dimensions of 150x150x4 mm. On each sample a thin layer of coating was applied. Three coatings were tested: RAL9005 black matte coating, LECHSYS 29141 Isolack black mat and white RAL 9010 matt. After application of the coatings, the samples were left to dry according to the specifications of the coating manufacturer. Before measuring the coating emissivity, the samples were left for two hours in a laboratory in order to equalize the temperatures of the samples and the environment. The initial thermograms at room temperature for each sample were recorded with infrared camera to determine the emissivity of each coating at room temperature. The exact temperature was measured by contact thermometer P410 with NiCr-Ni thermocouple (K type). Used contact thermometer had been calibrated, and the accuracy of temperature readings was within 0.1°C. The amount of sample temperature change during cold plastic deformation depends on the following factors: strain rate, reduction, the amount of used coolant and lubricant, friction, sample material, and some other factors of lower influence. From the experience of previous studies of plastic deformation at ambient temperatures, the amount of temperature change was about 60°C. Thus, it was planned to study the characteristics of coating emissivity in the range up to 110°C. Emissivity was determined at four temperatures. Sample heating is performed using a heater with temperature control. Each sample was heated up to a temperature of about 130°C. After that, the temperature of samples was gradually lowered, and at four different temperatures the temperature fields of samples were recorded with infrared camera. The exact values of temperatures during whole measuring time were measured simultaneously in selected points by the contact thermometer. The temperature readings were memorized. The described method is implemented for each selected coating. The emissivity for each measuring point was determined by the subsequent analysis of thermographic images. Analysis of thermographic measurements was performed using the software package Irbis3 professional.

RESULTS AND DISCUSSION

The samples from steel plate on which were applied the selected matt coatings are shown in Figure 1. After application of coatings and drying, on the samples at room temperature it was possible to see the differences between the coatings. Black matte coating RAL 9005 looked darker than Lechsys matte. However, comparing the samples with different coatings under the laboratory lighting it was possible to see the reflection from the lighting at RAL 9005 coating because of the colour fullness. Reflection was not expressed in case of Lechsys black matte coating and at white matte coating the reflection was not noticed. The temperature of samples was measured in several points by contact thermometer in order to confirm that temperature of samples is equal to ambient temperature of 16.5°C. After that, samples were recorded with the infrared camera to determine the emissivity for each coating. The samples were not touched with the hands to avoid their heating. In Figure 2 the thermographic image of sample with Lechsys matte coating at room temperature is shown.

Figure 1. Samples with chosen coatings

Figure 2. Thermographic display of sample with Lechsys matte coating at room temperature

Since the sample was at room temperature and coated with the coating of high emissivity, in Figure 2 it is almost impossible to distinguish the sample from the surroundings. This is proof that the temperature reading was accurate. After that, by the software package Irbis3 Professional the emissivity factors for each coating was determined, Table 1.

Table 1. Emissivity of tested coatings at 16,5 °C

Coating	Black matt RAL9005	Lechsys matt	White matt RAL9010
Emissivity	0.92	0.95	0.9

These measurements confirm that for the thermographic measurements Lechsys matte coating is more suitable because of higher emissivity compared to the other two coatings. Taking this into account and the fact that reflection of light was not noticed, Lechsys matte coating has better emission properties in relation to the other two coatings. The thermographic recordings of samples with Lechsys matte coating at different temperatures are shown in Figure 3.

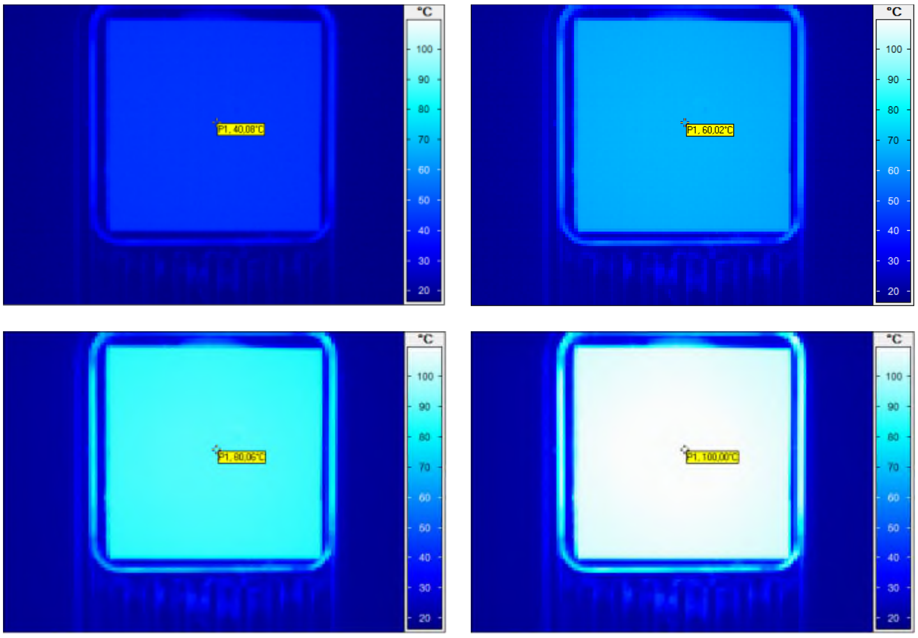

Figure 3. Thermograms of the sample with Lechsys black matte coating at different temperatures

By subsequent analysis with the software package Irbis3 Professional, it was found that the coatings had a certain changes in the value of the emissivity. This phenomenon could be explained by the differences in measured temperatures by the thermographic camera and the contact thermometer. Change the value of emissivity is not as significant, but generally falls with increase in temperature. By setting the emissivity inside the software package it was possible to obtain the same measured values. The measured values of emissivity are shown in Figure 4.

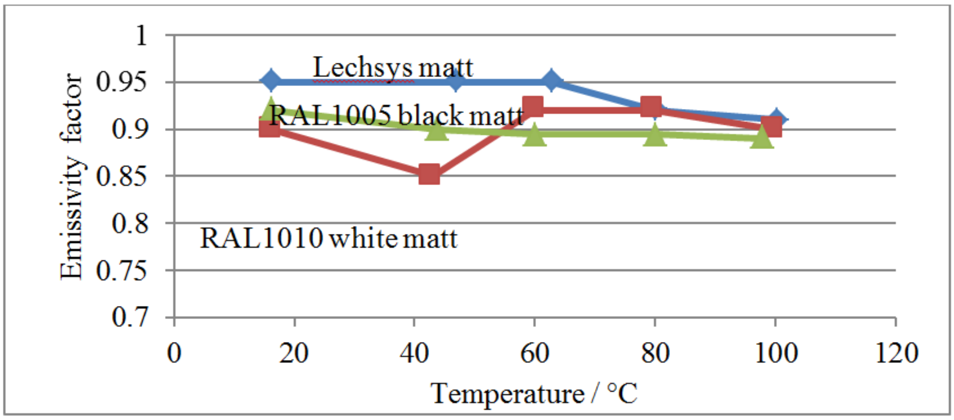

Figure 4. Change of coating emissivity with increase in temperature

From the measured values of emissivity, it can be seen that the smallest change is expressed in case of Lechsys black matte coating. The emissivity has constant value up to the temperature of 60°C, and then the emissivity falls. It may be noted that of all three coatings, Lechsys black mat has at all temperatures higher emissivity values. The RAL 1005 black matte coating also has a slightly monotonous decrease of emissivity with increase in temperature. The biggest change in emissivity has the white matte coating. At lower temperatures with temperature increase the emissivity falls, then increases even above the measured value at room temperature, and then again follows a slight decrease. The reason for this is a structural change in the material of coating, which affects the change in emission properties of the coating surface.

CONCLUSION

Research results show that there is a certain impact on the increase in temperature factor values of emissivity coatings investigated. Research results show that there is a certain impact of increase in temperature on the emissivity of tested coatings. The increase in temperature has the least impact on the emissivity of the two-component Lechsys black matte coating. A small drop in the value of emissivity was noticed only above 60 °C. The most significant influence of temperature on the value of emissivity was noticed in case of white matt coating, because of its structure changes with temperature rise. According to the research results from three tested coatings it is optimally to use the two-component Lechsys black matte coating for laboratory testing of cold plastic deformation. With a minimum change in the value of emissivity with increase in temperature, this coating also has no reflection at room temperature. Additionally it achieved the best adhesion on the sample surface, thus preventing its peeling during the sample deformation.

Acknowledgment

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REFERENCES

1. Mamuzić I., Drujan V. M., 1996, Teorija , materijali, tehnologija čeličnih cijevi, book, Hrvatsko metalurško društvo, Zagreb
2. M´Guil S., Wen W., Ahzi S., Gracio J.J., 2011, Modeling of large plastic deformation behavior and anisotropy evolution in cold rolled bcc steels using the viscoplastic-model-based grain-interaction, Mater. Sci. Eng. A, vol.528(18), 5840-5853
3. Su-Fen W., Yan P., Zhi-Jie L., 2013, Work-Hardening and Deformation Mechanism of Cold Rolled Low Carbon Steel, Res. J. Appl. Sci. Eng. Technol., vol.5(3), 823-828
4. Hodowany J., Ravichandran G., Rosakis A. J., Rosakis P., 2000, Partition of Plastic Work into Heat and Stored Energy in Metals, Experimental Mechanics, vol.40(2),113-123
5. Usamentiaga R., Venegas P. , Guerediaga J. , Vega L., Molleda J., Bulnes F. G., 2014, Infrared Thermography for Temperature Measurement and Non-Destructive Testing, Sensors 2014,vol.14, 12305-12348
6. Emissivity: Definition and Influence in Non-contact Temperature Measurement, , Accessible on Internet file:///C:/Users/ivanj/Downloads/py016emissivity-definition-and-influencee%20(1).pdf (25.01.2017.)
7. Jandrlić I., Rešković S., Lazić L., 2012, Značaj faktora emisivnosti kod termografskih ispitivanja plastičnosti čelika, Proceedings of 12th International Foundrymen Conference, Sustainable Development in Foundry Materials and Technologies, ur. N. Dolić, Z. Glavaš, Z. Zovko Brodarac, Metalurški fakultet, Opatija, 24.–25. svibanj 2012., 169-175.
8. Paloposki T., Liedquist L., 2005, Steel emissivity at high temperatures, Espoo 2005. VTT Tiedotteita - Research Notes 2299. 81 p.
9. Standard Test Methods for Measuring and Compensating for Emissivity Using Infrared Imaging Radiometers, ASTM E 1933 – 99a

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PROPERTIES OF ALKALI ACTIVATED SLAG UNDER THE SEAWATER ATTACK

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ABSTRACT

Electric arc furnace slag (EAFS) is used for synthesis of alkali activated slag (AAS). The samples of AAS were synthesized using the Na based and K based alkali activators.

Influence of alkali activator chemistry, *e.g.* influence of alkali ion (Na or K ion) on the durability of AAS in sea water was investigated. The results have shown that Na based AAS show a better durability in a sea water in comparison to K-AAS due to the lower porosity and sorptivity.

Key words: steel slag, alkali activation, sea water, durability, sorptivity.

INTRODUCTION

Alkali activation is new environmental friendly technology that enables transformation of waste material (metallurgical slag) into the useful product – alkali activated slag (AAS) which can successfully be used in civil engineering. The properties of AAS primarily depend on the choice of source materials. Mainly, blast furnace slag was used as a source materials but important shifts towards the use of other metallurgical slags like electric arc furnace slag was observed [1]. Electric arc furnace slag (EAFS), the by-product of steel production in electric arc furnace is mainly comprised of the Fe, Ca Al, Mg, Mn and P while the main crystal phases are dicalcium and tricalcium silicates, dicalcium ferrite and wüstite [2]. The AAS is produce by alkali activation process which involves a chemical reaction of slag with the alkaline activator [3]. Reaction product of slag alkali activation is calcium (alumino) silicate hydrate C–(A)–S–H gel with a low C/S ratio [4].

Besides the row materials selection, properties of AAS are greatly influenced by the alkali activator chemistry, *e.g.* by the choice of alkali ion used for a preparation of alkali activator.

Currently, AAS is now considers as an alternative to cementitous materials due to the enhanced durability in aggressive environment. The behaviour of AAS in sea water is important in terms of the ability of these materials to prevent harmful elements from sea water (chloride, magnesium, sulfate, and carbonate) from entering which can facilitate corrosion of steel bars and influence the structural capability of building elements [5].

In this paper, influence of alkali activator chemistry on the durability of AAS in sea water was investigated. The two samples of AAS, prepared using the Na based alkali activator and K based alkali activator were exposed to the sea water attack. Durability of AAS samples were evaluated from the standpoint of changes of mechanical properties.

EXPERIMENT

The EAFS used in this investigation was supplied from the Steel Mill Nikšić in Montenegro. Its chemical composition is given in the Table1.

Table 1. Chemical composition of EAFS

Component	CaO	FeO	SiO_2	Fe_2O_3	MgO	MnO	Cr_2O_3	Al_2O_3	TiO_2
Content / %	46.5	23.5	12.2	0.9	6.5	1.3	0.8	7.24	1.06

Table 2. Composition of alkali activators

Alkali activator	C(NaOH)	C(KOH)	$\frac{m(Na_2SiO_3)}{m(NaOH)}$	$\frac{m(Na_2SiO_3)}{m(NaOH)}$
Na-activator	10 M	-	2	-
K-activator	-	10 M	-	2

The AAS sample was synthesized using the powdered EAFS (d_{50}= 24μm) at a constant solid to liquid mass ratio of 4 using the two alkali activators, Na-activator and K-activator. Activators are prepared by mixing of MOH solution with the $M_2SiO_{3,}$ where M i Na or K ion (Table 2). Commercial Na_2SiO_3 (Na_2O = 8.5%, SiO_2 = 28.5%, density of 1.39 kg/m^3) and K_2SiO_3 (K_2O =13.18 %, SiO_2 = 26,38 %, density of 1.39 kg/m^3) solution are used for a preparation of alkali activator. The samples were denoted subsequently as Na-AAS and K-AAS according the type of activator used for their preparation.

The paste obtained by alkali activation was cast in a plastic cylindric mould and cured for 48 h at 65 °C. Subsequently, the AAS samples were removed from molds and left to stay an additional 4 weeks at ambient temperature.

Durability of Na-AAS and K-AAS in sea water was tested by immersing the samples in sea water for a period of 14 weeks. After this time, the samples were dried and subjected to the characterization tests.

The both, Na-AAS and K-AAS samples were subjected to porosity investigations using the ASAP 2020 instrument.

The capillary water absorption of Na-AAS and K-AAS was carried out according to the method described by Hall [6]. Cumulative water absorption per unit area of the inflow surface (*I)* is proportional to the square root of the elapsed time (*t*), (Eq. 1)

$$I = S\sqrt{t} \qquad (1)$$

The sorptivity coefficient (S) can be determined from the slope of the I *vs.* $t^{0.5}$ plot.

RESULTS AND DISCUSSION

The results of investigation given (Fig.1) have shown that mechanical properties of AAS samples are greatly influenced by the choice of alkali ion. It is evident that use of Na-activator lead to the strengthening of AAS samples. Na-AAS samples displayed the higher compressive strength in comparison to K-AAS samples. These results are in accordance with the results of porosity investigations (Fig. 1). Namely, the Na- AAS sample displayed the lower cumulative pore volume than K-AAS sample.

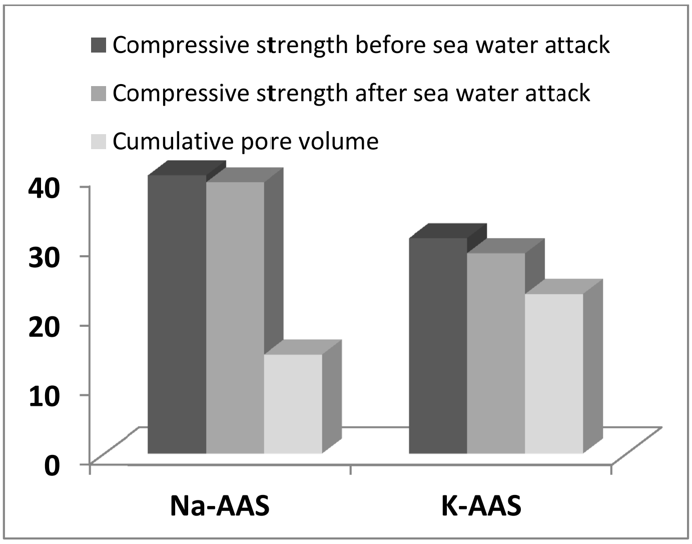

Figure.1. Compressive strength (MPa) and cumulative pore volume (mm^3g^{-1}) of Na- AAS and K-AAS samples

After the immersion in sea water for a period of 14 weeks, the both samples displayed the certain strength loss. The Na-AAS sample displayed only slight strength loss 2.5 % while the K-AAS sample displayed the higher strength loss of 6.9 %.

Immersing Na-AAS and K-AAS in sea water generates alkaline solution (pH = 9.6) due to the ion exchange between the excess of Na^+ or K^+ from AAS matrix and

H_3O^+ from the aquatic environment [7]. Microstructural investigations have shown the formation of protective layer (A) on the surface (B) of both, Na-AAS and K-AAS immersed in seawater (Fig. 2).This layer acts as a barrier and slows down the penetration of chloride ions inside the Na-AAS and K-AAS protecting them from the aggressive environment.

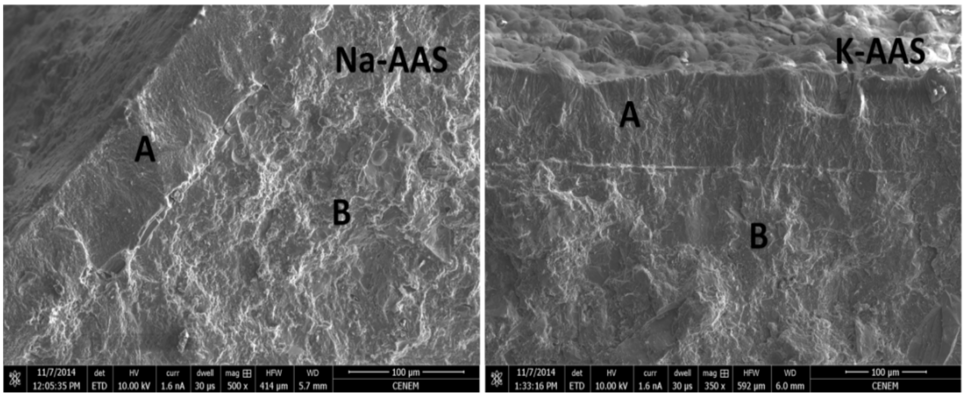

Figure 2. Microstructure of Na- and K-AAS samples before and after the seawater attack

Derogation of mechanical properties of AAS sample after immersion in sea water can be explained by the decomposition of reaction product of slag alkali activation (C–(A)–S–H gel) due to the sea water attack which lead to decalcification of the C–A–S–H phase [5]. In the same time Mg^{2+} ions from sea water attack decalcified C–(A)–S–H which led to the formation of a non-cementing magnesium silicate hydrate (M–(A)–S–H) by an ion exchange between Mg^{2+} and Ca^{2+} ions in the C–(A)–S–H) [5]. Additionally, Mg^{2+} present in the sea water precipitate at the surface of AAS as $Mg(OH)_2$ due to the alkalinity of solution and form the protective layer [7].

Stability of building materials in sea water is determined by the rate of water uptake by matrix when exposed to sea water *i.e.* by the sorptivity of matrix which enables the transport of sea water and entering the harmful elements into materials interior.

The calculated sorptivity coefficients (*S*) according the Hall method [**Error! Bookmark not defined.**], for Na-AAS and K-AAS are given in Fig. 3. The results of capillary water absorption tests indicate that sorptivity of Na-AAS is lower than that of K-AAS which is in agreement with the lower porosity and lower strength loss of Na-AAS samples after the sea water attack due to the lower water uptake and ingress of harmful elements.

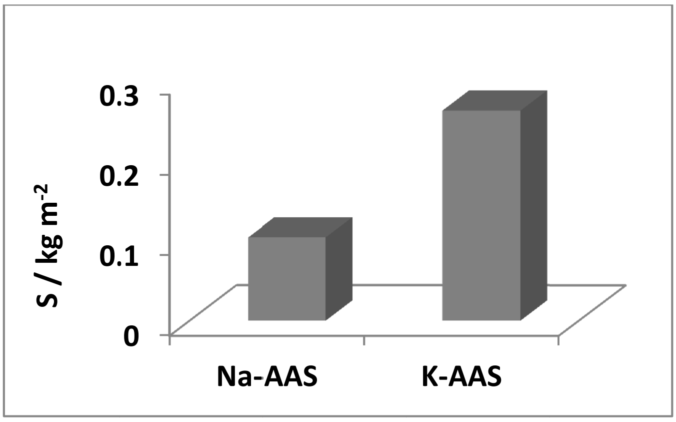

Figure 3. Sorptivity coefficients (S) of Na-AAS and K-AAS samples.

CONCLUSIONS

The next conclusions can be drawn on the basis of the results of investigations:

- Use of Na-activator promotes the strengthening of AAS sample.
- Na-AAS sample displayed the higher compressive strength in comparison to K-AAS due to the lower porosity of Na-AAS.
- The lower porosity of Na-AAS sample led to the better durability of Na-AAS sample in a sea water in comparison to K-AAS sample due to the lower sorptivity.

REFERENCES

1. Nikolić, I. Karanović, LJ., Častvan, I.J, Radmilović, V., Mentus, S., Radmilović, V. (2014) Improved compressive strength of alkali activated slag upon heating, Mater. Lett. 133 251–254.
2. Sofilić, T., Merle, V., Rastovčan-Mioč, A., Ćosić, M., Sofilić, U., (2010) Steel slag instead natural aggregate in asphalt mixture. Arch Metall Mater,55:657–68.
3. Krizan, D., Zivanovic, B. (2002) Effects of dosage and modulus of water glass on early hydration of alkali-slag cements. Cem Concr Res, 32:1181–8.
4. Chen, W., Brouwers, HJH., (2007)The hydration of slag, part 1: Reaction models for alkali-activated slag. J Mater Sci,42:428–43.
5. De Weerdt, K., Justnes ,H., (2015) The effect of sea water on the phase assemblage of hydrated cement paste. Cem Concr Compos, 55:215–22
6. Hall, C., (1989)Water sorptivity of mortars and concretes: a review. Mag Concr Res 41:51–61.
7. Aly, Z., Vance, ER., Perera, DS., Hanna, J V., Griffith, CS, Davis, J., (2008) Aqueous leachability of metakaolin-based geopolymers with molar ratios of Si/Al=1.5–4. J Nucl Mater, 378:172–9.

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KINETIC STUDY OF Cu(II) AND Zn(II) IONS SORPTION ONTO RECYCLED CONCRETE

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ABSTRACT

The possibility of aged concrete fines reuse was explored through its application as a matrix for heavy metal ions separation from aqueous media. The Cu(II) and Zn(II) sorption kinetics onto concrete particles was explored, in the series of experiments conducted in batch conditions. Higher tendency of Zn(II) to bond onto mineral surface was observed considering single component solutions, whereas Cu(II) removal was more efficient from equimolar binary mixtures. Experimental data were described using pseudo-second order kinetic model. The results point to the possible utilization of crushed concrete as a component of water protection and purification systems.

Key words: concrete, sorption, Cu(II), Zn(II), kinetic modeling .

INTRODUCTION

High amounts of construction and demolition waste (C&DW) are generated continuously on a global level, raising the necessity for development of new technologies for recycling of such materials. C&DW is consisted of numerous components such as bricks, wood, wool, asphalt, concrete, plastics, etc. Among them, concrete is the most often used construction material in the last decades, with the contribution of approximately 40% of the total amount of waste produced by the demolition of ruined buildings. Various investigations on aged concrete usability as filler in the fresh concrete preparation were reported [1]. Furthermore, it was used for acidic wastewater neutralization due its high alkalinity [2], but also for the removal of pollutants, especially phosphates. The study of Cu^{2+}, Zn^{2+} and Pb^{2+} ions sorption from aqueous solutions onto crushed concrete has revealed that it has the promising capacity to retain selected cations [3]. The concrete samples used in the referred work were freshly prepared and crushed after solidification. However, the utilization of aged concrete for the waste waters purification has not been investigated so far.

In this study, Zn(II) and Cu(II) ions sorption onto waste concrete was explored. These metals were chosen based on their toxicity and frequent occurrence in industrial wastewaters and acid mine drainages [4].

The main aim of this study was to investigate the kinetics of Cu(II) and Zn(II) ions separation by concrete fines, in order to explore the performance of this type of waste, the equilibration time and the sorption capacities for selected heavy metal cations from both single component solutions and equimolar binary mixture.

MATERIALS AND METHODS

For the simulation of wastewaters containing Cu(II) and Zn(II) ions, the synthetic aqueous solutions were prepared from Cu(II) and Zn(II) nitrate salts (Merck, p.a. purity) and deionized water. The initial concentration of metals in single component solutions was $2 \cdot 10^{-3}$ mol/L, which was also the total concentration of both metal cations in equimolar mixture. The pH values of prepared working solutions were 5.5.

Concrete samples were collected from the ruined buildings, dating back to 1970's. The representative sample was made from several subsamples, and then crushed, homogenized and sieved. Fraction of the particle size < 250 μm was used in the sorption experiments.

Sorption kinetics was investigated in the series of separate batches, using 0.1 g of concrete sample and 20 mL of solutions containing chosen metals. Obtained suspensions were mixed in the rotary shaker at 10 rpm, at 20°C. Contact time was varied from 15 min to 24 h. After specified contact time, one of the batches was taken for solid/liquid separation by centrifugation (9000 rpm, 10 min.).

The concentrations of metal ions in the solutions before and after sorption were determined using Atomic Absorption Spectrophotometer (Perkin Elmer 3100 AAS). In addition, filtrate pH values were monitored using WTW InoLab pH-meter.

RESULTS AND DISCUSSION

The kinetic curves, showing metal ions sorption from single component solutions, are presented in Fig.1a. The increase in contact time provoked the increase of sorbed amounts of both cations. The process was fast at the beginning, while for the longer contact times it slowed down until the equilibrium was reached. The time of reaction necessary for achieving the equilibrium was approximately 1h in the system with Zn(II) ions. The sorption capacity of concrete toward Zn(II) ions was 0.36 mmol/g. Comparing sorption kinetics from single metal solutions, Cu(II) removal was slower and less efficient. Equilibrium sorption was reached after 2 h of contact and the corresponding sorption capacity was 0.21 mmol/g.

Measured pH values were relatively constant during metal removal process (Fig. 1a.). In the system with Cu(II) ions pH was 6.2 ± 0.1, whereas higher pH values were characteristic for Zn(II) sorption (7.3 - 7.9).

The reversal of concrete selectivity has been noticed considering binary solutions (Fig. 1b), i.e. sorption of Cu(II) ions was more efficient in respect to Zn(II) species. pH values, measured after specified contact times, were constant (6.4 ± 0.1). Relatively constant pH values observed during the sorption indicate that the mineral matrix of explored material exhibit high buffering potential. After 24 h of contact, the sorbed amounts of Cu(II) and Zn(II) ions were found to be 0.13 mmol/g and 0.019 mmol/g, respectively, which signifies reduced metal removal capacity in competitive conditions. Furthermore, the sorption rate for both cations decreased compared to kinetics of sorption from single component solutions. The equilibrium removal of Zn(II) ions was attained after 6h, while the sorption of Cu(II) constantly increased during the course of the experiment.

The experimental data were fitted by pseudo-second order kinetic model, which was broadly used to describe the kinetics of sorption of divalent metals from aqueous solutions on various solid materials [5]:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \qquad \text{(Eq. 1)}$$

In Eq. 1, t (h) is the contact time, q_t and q_e (mmol/g) are sorbed amounts of cations at time t and at equilibrium, respectively, while k_2 (g/mmol h) is the pseudo-second order rate constant. From linear dependences t/q_t vs. t, the values of q_e and k_2 were calculated. The numerical value of initial sorption rate h (mmol/g h) is equal to the inverse intercept value. Calculated parameters q_e, k_2 and h, as well as determination coefficients (R^2), are given in Table 1.

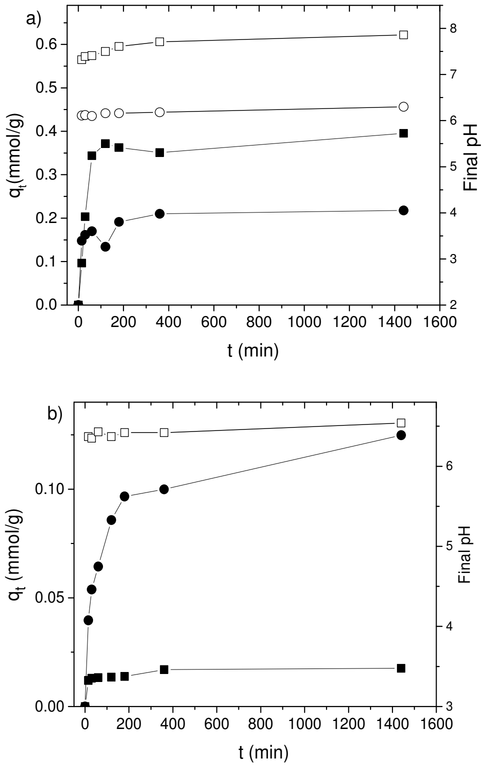

Figure 1. Sorption kinetics of Zn (II) (■) and Cu(II) (●) ions onto waste concrete fines, from (a) single-component solution, and (b) equimolar bi-component solutions.
Open symbols represents measured final pH values.

Excellent agreement with the model was obtained for Zn(II) sorption from single component solution and Cu(II) sorption from the binary mixture, while, in other systems, the implementation of this model was less adequate. Calculated equilibrium sorbed quantities were close to values obtained experimentally. Matching values of calculated and experimentally obtained q_e values for Cu(II) removal out of binary mixture, indicate that 24 h of contact was probably enough to attain the equilibrium. The highest and the lowest values of initial sorption rates were characteristic for Zn(II) ions sorption from the single and binary solution, respectively. This is in agreement with the fast Zn(II) sorption from single metal solution. Otherwise, extremely low value for h, but also low q_e observed for Zn(II) in the multi-component solution suggested that the existence of Cu(II) ions in the solution diminished Zn (II) bonding.

Table 1. Pseudo-second order kinetic parameters calculated for Cu(II)and Zn(II) sorption from single and bi-component solutions onto waste concrete fines.

		q_e (mmol/g)	**k_2 (g/mmol h)**	**h mmol/g h**	**R^2**
Single component solution	**Zn**(II)	0.401	0.090	$1.40 \cdot 10^{-2}$	0.999
	Cu(II)	0.205	0.027	$1.12 \cdot 10^{-3}$	0.891
Bi-component mixture	**Zn**(II)	0.0228	0.094	$4.91 \cdot 10^{-5}$	0.641
	Cu(II)	0.129	0.13	$2.22 \cdot 10^{-3}$	0.999

The agreement between experimental results and pseudo-second order kinetic model provides the prediction of sorption capacity, however, without information about operating sorption mechanism. Even more, this model was found to be suitable for the description of sorption processes which occur via different mechanisms, for example ion-exchange, precipitation, surface complexation, etc. Consequently, it was found to be suitable for the description of Cu(II) and Zn(II) sorption kinetics onto such diverse materials as bentonite [6], sugar beet pulp and fungus *Mucor rouxi* [7].

In order to understand the investigated process, it must be taken into account that concrete is composed of sand (SiO_2), water and cement (SiO_2, CaO, Fe, Al, K, Na oxides, etc.). The main minerals in freshly prepared concrete are calcium silicate hydrates (C-S-H), calcium aluminate hydrates, and calcium aluminosilicate hydrates. However, the exposure of concrete to atmospheric conditions (heating–cooling cycles, cosmic radiation, reactions with CO_2 and other atmospheric gases, reactions with atmospheric precipitation, etc.,) largely contribute to the aging process. As a consequence, decalcifications of C-S-H occurs, as well as silicates polymerization, which results in SiO_2 and carbonates as final products, with high content of free calcium and with high alkalinity [8]. Furthermore, the presence of Fe-compounds in concrete samples is common due to addition of calcium alumino ferrites during cement production [9].

In previous investigations on Cu(II) ions sorption by amorphous silica [10] or α-$SiO_{2,}$[11] bonding of copper ions was found to occur dominantly by inner-sphere complexes formation, especially by forming monomer and dimmer complexes, or by precipitation [12].

The affinities of various solid matrices toward Cu(II) and Zn(II) ions have variable sequences. For example, considering single metal solutions, more efficient sorption of Zn(II) in respect to Cu(II) was observed using bentonite [13]. The authors have noticed that the ion-exchange mechanism was dominant for the sorption of aforementioned cations. On the other hand, Park et al. [14] have investigated sorption of Pb, Zn, Cu, Cr and Cd onto sesame straw biochar, with more promising results for Cu(II) than for Zn(II) ions removal, considering single and multi-metal solutions. The preferential sorption of Zn(II) was explained in literature by cation-exchange theory, while preferential retention of Cu(II) in respect to Zn(II) was attributed to the differences in their electronegativity [14]. In addition, competitive sorption of Pb, Zn, Cu, Cr and Cd onto clay bearing wastes was investigated [15]. Various natural and synthetic minerals retain Pb and Cu ions more strongly than Zn, Cd and Ni, furthermore, Fe-oxides, organic and carbonate fraction of the soil matrix exhibit higher tendency to bond Cu(II) than Zn(II) ions [15, 16].

Considering the results of this study, higher affinity of waste concrete sample toward Zn(II) ions in single-component experiments, can be explained only by higher final pH values measured in Zn(II)-concrete system (Fig. 1a), which may result in high degree of hydrolysis and surface precipitation of Zn ions.

Accordingly, waste concrete fines potential for removal of Zn(II) and Cu(II) ions is a result of a complex mechanism, which may include surface complexation, precipitation and ion-exchange. The complexity of the process is provoked by different minerals contained in the concrete, but also by the properties of cations and their ionic-species distribution highly dependent on pH. Furthermore, beside sorption affinity and low cost, concrete fines loaded with heavy metals can be utilized as an additive in fresh concrete preparation in some specific applications. In this way, the 3R rule of sustainable development (Reduce, Reuse, Recycle) would be satisfied.

CONCLUSION

The sorption of Cu(II) and Zn(II) ions onto aged concrete sample was investigated in order to explore and compare the rates and the capacities of such waste material towards different pollutants. The investigation of process kinetics from single-component solutions have revealed more efficient and faster removal of Zn(II) ions in respect to Cu(II), which can be contributed to the higher pH values in Zn-concrete system. Quite the opposite, the surface of concrete sample became more selective towards Cu(II) ions when equimolar two-component solution was considered. The sorption rates and the capacities of both metal cations were affected in terms of competition, however, Zn (II) ions removal was more suppressed. Based on the obtained results, aged concrete is a component of construction and demolition waste capable for heavy metal ions immobilization. In such processes, alkaline nature and buffering capacity of concrete are the important features. The performance of waste concrete and other categories of C&DW need to be evaluated under different experimental conditions, in order to realize the perspective of their implementation in water purification technologies.

Acknowledgement

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REFERENCES

1. Oikonomou N.D, Recycled concrete aggregates, Cem. Concr. Compos. 27: 315–318, 2005.
2. Raclavská H., D., M., Škrobánková H., Potential utilization of crushed concrete in the acid mine drainage treatment, in: 12th Conference on Environment and Mineral Processing. Part III. VŠB- Technical University, Ostrava, pp. 147–154, 2008.
3. Coleman N.J., Lee W.E., Slipper I.J., Interactions of aqueous Cu^{2+}, Zn^{2+} and Pb^{2+} ions with crushed concrete fines. J. Hazard. Mater. 121: 203–213, 2005.
4. Tiller K.G., Hodgson T.J.,The specific sorption of cobalt and zinc by layer silicates, Clays Clay Miner. 9: 393–403, 1960.
5. Ho Y., McKay G., Pseudo-second order model for sorption processes, Process Biochem. 34: 451–465, 1999.
6. Veli S., Alyüz B., Adsorption of copper and zinc from aqueous solutions by using natural clay, J. Hazard. Mater. 196: 226-233, 2007.
7. Ho Y.S., Review of second-order models for adsorption systems, J. Hazard. Mater. 136: 681-689, 2006.
8. Black L., Garbev K., Gee I., Surface carbonation of synthetic C-S-H samples: A comparison between fresh and aged C-S-H using X-ray photoelectron spectroscopy, Cem. Concr. Res. 38: 745–750, 2008.
9. Ochs M., Mallants D., Wang L., Radionuclide and Metal Sorption on Cement and Concrete, Springer International Publishing, 2016.
10. Cheah S.-F., Brown G.E., Parks G.A., XAFS spectroscopy study of Cu(II) sorption on amorphous SiO_2 and γ-Al_2O_3: Effect of substrate and time on sorption complexes, J. Colloid Interface Sci. 208: 110–128, 1998.
11. Šljivić M., Smičiklas I., Pejanović S., Plećaš I., Comparative study of Cu^{2+} adsorption on a zeolite, a clay and a diatomite from Serbia, Appl. Clay Sci. 43: 33–40, 2009.
12. Brown G., Parks G., Sorption of trace elements onto mineral surfaces: modern perspectives from spectroscopic studies, and comments on sorption in the marine environment, Int. Geol. Rev. 43: 963–1073, 2001.
13. Kubilay Ş., Gürkan R., Savran A., Şahan T., Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite, Adsorption. 13: 41-51, 2007.
14. Park J.H., Ok Y.S., Kim S.H., Cho J.S., Heo J.S., Delaune R.D., Seo D.C., Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions, Chemosphere. 142 : 77-83, 2016.
15. Helios-Rybicka E., Wójcik R., Competitive sorption/desorption of Zn, Cd, Pb, Ni, Cu, and Cr by clay-bearing mining wastes, Appl. Clay Sci. 65: 6–13, 2012.
16. Fontes M.P.F., Gomes P.C., Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils, Appl. Geochemistry. 18: 795–804, 2003.

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MONITORING OF HEAVY METALS CONTENT IN SOIL COLLECTED FROM SMELTER-POLLUTED AREA, SERBIA

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ABSTRACT

This papers deals with the assessment of heavy metals in soil collected in the village Slatina near Bor, where mining and matallurgical activities have had a significant impact on the environment. A total of 20 soil samples were collected and analyzed for six heavy metals. The levels of Cu, Ni, Pb, Zn, Cr and Hg have been determined by Microwave Plasma Atomic Emission Spectroscopy (MP-AES). The collected data was processed and analysed in accordance with the Legistation of the Republic of Serbia.

Key words: heavy metals, soil pollution.

INTRODUCTION

Heavy metals are naturally present in soil, contamination comes from anthropogenic activities such as industrial activities, the application of agricultural chemicals, the improper disposal of waste, combustion of fossil fuels and road traffic [1-4]. Soil pollution with heavy metals is a significant environmental problem in the entire world [5,6]. The most important sources of heavy metals in the environment are mining and metallurgical industries [7]. Long-range transport of atmospheric pollutants adds to the metals in the natural environment [8,9].

Accumulation of heavy metals in the soil can affect soil activity, reduce crop yield and harm the safety of agricultural products, and thus negatively impact the health of human and animals, including the ecosystem [10-12].

MATERIAL AND METODS

Figure 1 presented the location of the samling site with measuring points. Soil samples were collected at surface level (0-25 cm in depth). Description of sampling sites is presented in table 1.

Safety at work and environmental protection ″Beograd″ d.o.o. measured the soli quality in Slatina - ″Report on the Soil Quality in Slatina, Bor″, October 2015.

Figure 1. Location of the samling site with measuring points – Slatina

Table 1. Description of sampling sites

Sample (code)	**GPS coordinates**	**Sample (code)**	**GPS coordinates**	**Sample (code)**	**GPS coordinates**	**Sample (code)**	**GPS coordinates**
ZBRD1	N $44^0$02′33.98″ E $22^0$09′37.63″	ZBRD4	N $44^0$02′09.42″ E $22^0$10′25.60″	ZBRD3	N $44^0$02′14.92″ E $22^0$10′13.47″	ZBRL5	N $44^0$02′45.65″ E $22^0$09′23.26″
ZBRL1	N $44^0$02′35.10″ E $22^0$09′37.82″	ZS3	N $44^0$02′38.63″ E $22^0$09′40.50″	ZBRL3	N $44^0$02′17.85″ E $22^0$10′14.47″	ZS4	N $44^0$02′30.42″ E $22^0$09′32.19″
ZBRD2	N $44^0$02′24.35″ E $22^0$09′56.94″	ZS5	N $44^0$02′29.31″ E $22^0$09′56.61″	ZS1	N $44^0$02′26.15″ E $22^0$09′40.98″	ZS6	N $44^0$02′20.49″ E $22^0$09′54.76″
ZBRL2	N $44^0$02′25.33″ E $22^0$09′57.48″	ZS7	N $44^0$02′20.75″ E $22^0$10′19.74″	ZS2	N $44^0$02′07.30″ E $22^0$09′34.00″	ZS8	N $44^0$02′11.47″ E $22^0$10′11.05″
ZR1	N $44^0$05′45.07″ E $22^0$06′35.14″	ZS9	N $44^0$02′04.21″ E $22^0$10′28.24″	ZBRL4	N $44^0$02′10.23″ E $22^0$10′26.59″	ZS10	N $44^0$02′23.97″ E $22^0$10′25.57″

The soil sampling procedure has been established according to the standard:
ISO 10381-1:2002 Soil quality- Sampling-Part 1: Guidance on the design of sampling programs;
ISO 10381-2:2002 Soil quality- Sampling-Part 2: Guidance on sampling techniques;
ISO 10381-3:2002 Soil quality- Sampling-Part 3: Guidance on safety;
ISO 10381-4:2002 Soil quality- Sampling-Part 4: Guidance on the procedure for investigation of natural, near-natural and cultivated sites;
ISO 10381-5:2002 Soil quality- Sampling-Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soli contamination;
ISO 10381-6:2002 Soil quality- Sampling-Part 6: Guidance on collection, handling and storage of soil under aerobic condition for the assesssment of microbiological processes, biomass and diversity in the laborotory.

Microwave Plasma Atomic Emission Spectroscopy (MP-AES) method was used for determining the concentration of Cu, Ni, Pb, Zn, Cr, Hg, pursuant to the VDM 26 – Aplication Note – Determination of metals in soil using the 4100 MP-AES, Agilent Trchnologies, Melbourne, Australia.

The collected data was processed and analysed in accordance with the Regulation on a program of systematic monitoring of soil quality indicators for assessing the risk of soil degradation and methodology for development of remediation programs (Offical Gazette RS no.88/2010) and Regulation on the permitted amounts of hazardous and harmful substance in soil and water for irrigarion and methods of their testing (Offical Gazette RS no.23/94).

Table 2. Soil qualitu – Standards and Guidelines

Parameter / Heavy metals, mg/kg	MDK in soil, mg/kg (*Offical Gazette RS no.23/94)*	Soil (mg/kg absolutely dry matters) *Offical Gazette RS no.88/10*	
		Limit value	Remediation value
Lead, Pb	100	85	530
Zink, Zn	300	140	720
Copper, Cu	100	36	190
Chrome, Cr	100	100	380
Nickel, Ni	50	35	210
Mercury, Hg	2	0,3	10

RESULTS AND DISCUSSION

Concentration of Cu, Ni, Pb, Zn, Cr and Hg in soil, were calculated from data obtained from 20 soil samples collected in Slatina (ZS9, ZBRD4, ZBRL4, ZS7, ZBRL3, ZS8, ZBRD3, ZS10, ZS1, ZBRD1, ZS4, ZS2, ZS6, ZR1, ZBRL1, ZS5, ZBRL5, ZBRL2, ZS3,ZBRD2) and presented in figute 2-9.

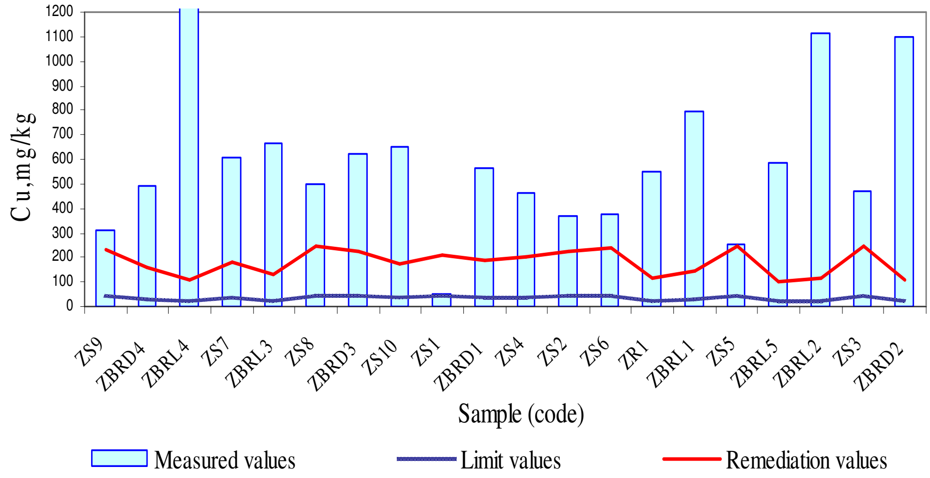

Figure 2. Concentration of Cu, mg/kg from soil samples collected in Slatina

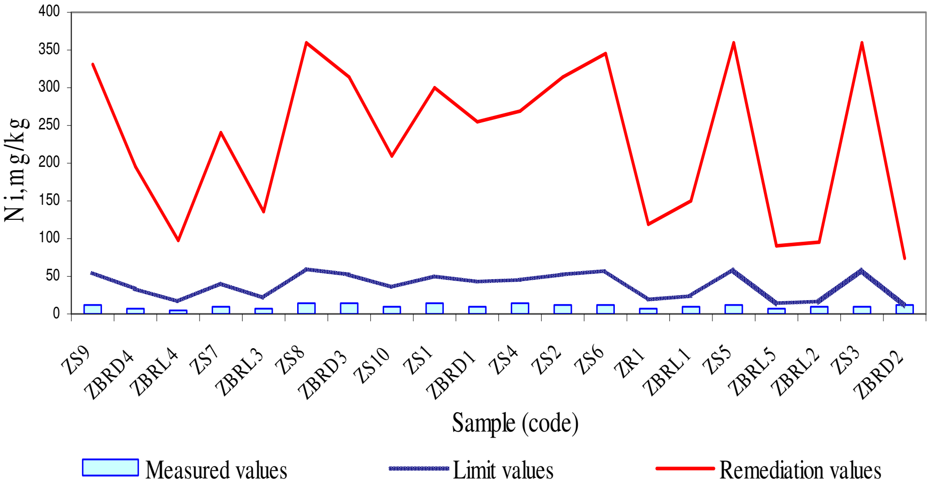

Figure 3. Concentration of Ni, mg/kg from soil samples collected in Slatina

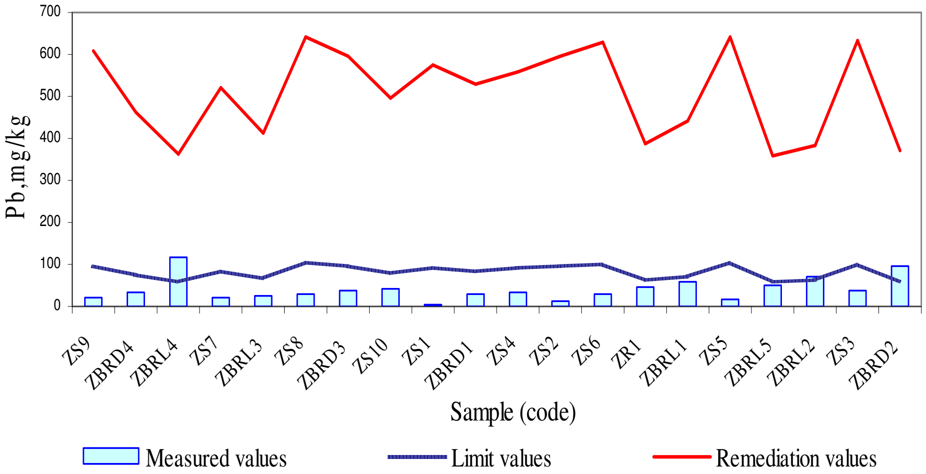

Figure 4. Concentration of Pb, mg/kg from soil samples collected in Slatina

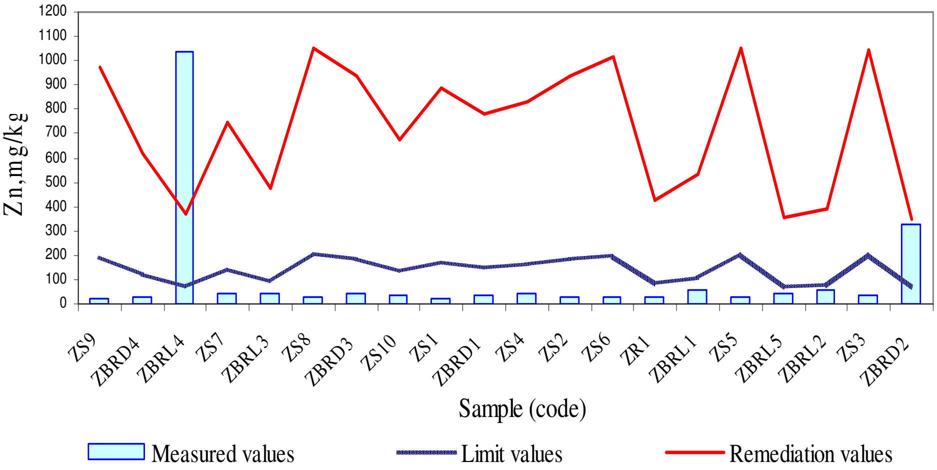

Figure 5. Concentration of Zn, mg/kg from soil samples collected in Slatina

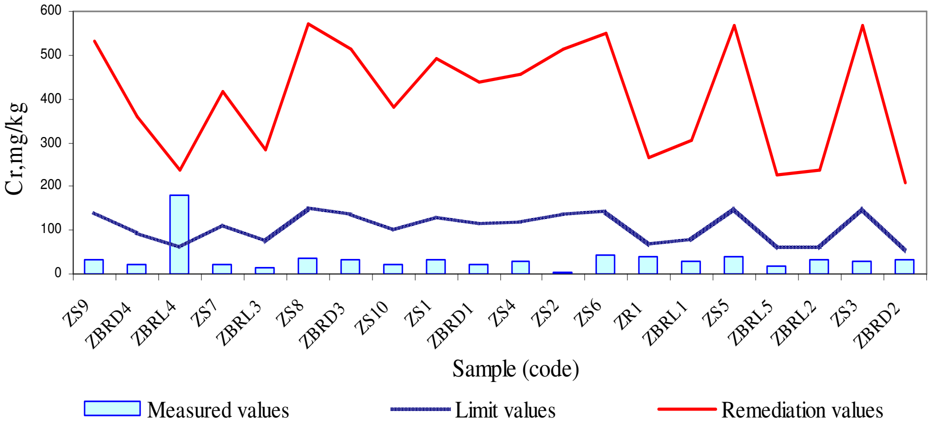

Figure 6. Concentration of Cr, mg/kg from soil samples collected in Slatina

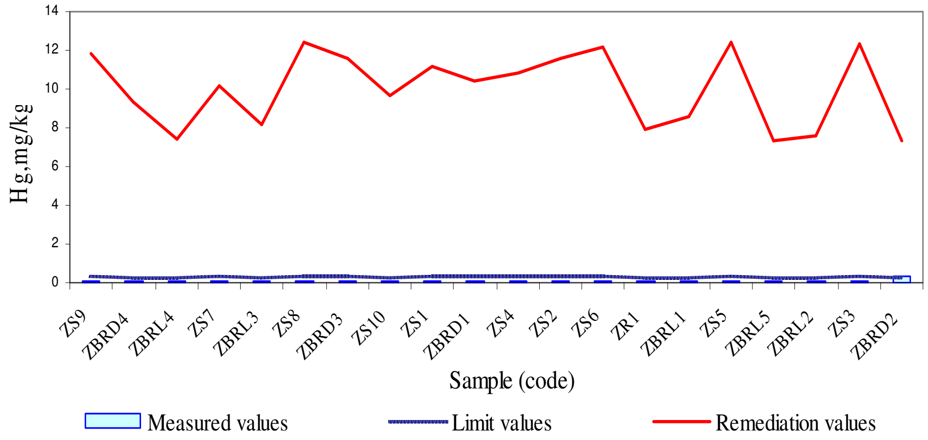

Figure 7. Concentration of Hg, mg/kg from soil samples collected in Slatina

CONCLUSION

Through the analysis of 20 soil samples of this studa area, can be concluded that remediation values are exceeded for copper, as a result of long-term impacts of mining and metallurgical activities and outdated technologies for copper production. Sample ZBRL4 indicates that the soil is contaminated with Zn. The rest of the samples did not exceeding remediation values.

Implementation of remediation programs, based on the laws, rules and guidance, through cleanup programs, will be achieved by removal or in-situ treatment of contamination.

Applying BAT technology within the New Flash Smelting and Sulphuric Acid plant will significantly impact the environment.

REFERENCES

1. Romic M., Romic D., 2003. Heavy metals distribution in agricultural topsoils in urban area. Environmental Geology 43(7):795–805.
2. Wei B., Yang L., 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils fromChina. Microchemical Journal 94(2):99–107.
3. Yaylalı-Abanuz G., 2011. Heavy metal contamination of surface soil around Gebze industrial area, Turkey. Microchemical Journal 99(1):82–92.
4. Zhao Y., Xu X., Sun W., Huang B., Darilek JL., Shi X., 2008. Uncertainty assessment of mapping mercury contaminated soils of a rapidly industrializing city in the Yangtze River Delta of China using sequential indicator cosimulation. Environmental Monitoring and Assessment 138(1–3): 343–355.
5. Dragovic S., Mihailovic N., Gajic B., 2008. Heavy metals in soils: distribution, relationship with soil characteristics and radionuclides and multivariate assessment contamination sources. Chemosphere, 72(3): 491–495.
6. Hu Y., Liu K., Bai J., Shih K.,. Zeng E.Y, Cheng H., 2013. Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. Environmental Science and Pollution Research 20(9): 6150–6159.
7. Korać M., Kamberović Ž., 2007. Characterization of wastewater streams from Bor site. Metallurgical & Materials Engineering 13 (1): 41-52.
8. Šerbula S., Antonijević M., Bogdanović G., Milić S., Jovanović B., Solid particles as air pollutant, In Proceedings 15th International Scientific and Professional Meeting Ecological Truth, ECOIST'07. Eds.: M. Trumić, University of Belgrade, Technical Faculty Bor, Sokobanja (Serbia), 27-30. May 2007, p.360-364.
9. Jovanović B., Todorović B., Atmospheric particulate matter concentration and their heavy metal content in Bor (Serbia), In Proceedings XXIV International Conference Ecological Truth, ECOIST'16. Eds.: R.V.Pantović, Z.S.Marković, University of Belgrade, Technical Faculty Bor, Vrnjačka banja, (Serbia), 12.-15. June 2016 p.84-90.
10. W. de Vries, P. F. Römkens, and G. Schütze, 2007. Critical soil concentrations of cadmium, lead, and mercury in view of health effects on humans and animals. Reviews of Environmental Contamination and Toxicology 191: 91–130.
11. Nagajyoti P.C., Lee K.D., Sreekanth T.V.M. , 2010. Heavy metals, occurrence and toxicity for plants: a review. Environmental Chemistry Letters 8(3):199–216.
12. Chen H., Teng Y., Lu S., Wang Y., Wang J., 2015. Contamination features and health risk of soil heavy metals in China. Science of the Total Environment 512–513:143–153

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STUDY ON DETERMINING ACCIDENTAL EMISSIONS OF TOXIC, ASFIXIANT FLAMMABLE OR EXPLOSIVE GASES, VAPORS AND DUSTS IN EXPLOITATION OF COOPER ORE

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ABSTRACT

The paper presents the technical data and information of workplaces within a Romanian copper mine, in order to identify accidental emissions of toxic, asphyxiating, flammable or explosive gases, vapours and dusts. Thus, after a synthesis of the activities and working technologies, we present the results found after analyzing and checking the existing risk factors that can cause catastrophic situations on the environment.

Explosives are mainly used in the above-ground extractive industry (quarries) for exploitation of various deposits of useful mining substances. The techniques most used are those that involving mine holes or bore holes. Irrespective of explosives used detonation of explosives for civil use discharges gases and noise in the atmosphere, polluting the environment, and, in time, may affect the health of population in neighbouring areas.

Key words: environment, pollution, gas, ore, health, explosives for civil use.

INTRODUCTION

Many technological processes imply certain risks in their exploitation. Increasing the size and complexity of technological processes, development of new technological processes and manufacturing technologies in various industries, in addition to multiple and important benefits, also generates negative effects. Losses generated by these processes can occur both in normal operation and also in the event of an accident or abnormal operation of technical and technological systems.

From a qualitative point of view, ***technical security*** represents the ability of technical systems to avoid damage to health or loss of people's lives, loss of material damage and damage or loss to the environment caused by faulty operation.

Major accidents that can occur at an industrial site are explosions, fires and toxic emissions. The consequences of such accidents can be serious, even catastrophic, generally resulting in human losses, "ecological" damage to the natural environment and damage to property.

COPPER ORE PRODUCTION TECHNOLOGY

The extraction of copper ore is carried out in quarries (fig. 1), using as working technology the following phases: uncovering the areas to be exploited, performing the trough-cuts, drilling boreholes, loading them with explosive material, detonation, loading the blasted material, transporting the blasted material. After the extraction process follows the transportation of the usable material to the crushing plant and ore preparation in the preparation plant.

Figure 1. General view

In the preparation plant, the operations ore is subjected to the following processes: primary crushing, grinding, grading, flotation, drainage of cupriferous concentrate by thickening and filtration, thickening, transport and storage of tailings in sludge beds.

Selective flotation of cupriferous ore is performed in 17m^3 pneumo-mechanical cells (fig. 2), followed by two re-flotation of the primary concentrate.

Figure 2. Pneumo-mechanical cells

The flotation process uses two types of reagents:

- **Collector reagents** (organic substances absorbed on mineral surface increasing it's hydrophobicity);
- **Foaming reagents** (surface-active organic surfaces absorbed at the surface of air bubbles lending them stability and strength)

Taking into account the physical - mechanical properties of the rocks in the studied quarry, the bore holes are placed in a square network of 6-7 m at the through-cut, respectively of 4-5 m at the ore.

Chemicals used in the flotation process, respectively collector and sponge, may pose a risk to workers in the event of improper handling and non-use of personal protective equipment. According to the technical data sheets, they present a danger to human / health in case of inhalation, swallowing, irritation, chemical burns, being the use of respiratory protective equipment recommended.

BLASTING WITH EXPLOSIVES

The aspects to be considered when choosing explosive blasting technology are: the physical-mechanical properties of rocks to be dislodged, field topography in the area of exploitation benches, micro tectonics of the area, quarry geometry and technical equipment available.

Through drilling - explosive loading – blasting a 90mx23mxl5m bench block (panel), a volume of 31,050 m^3 is obtained, for which a length 735 m of borehole is drilled.

Because explosives are used, there are explosive warehouses in every quarry. All of them hold permits for the preparation, possession, transport, sale and use of explosive materials issued by the Territorial Labour Inspectorates and by the County Police Inspectorate where the warehouse is located.

PHYSICAL AND CHEMICAL BEHAVIOUR OF THE MAIN DANGEROUS SUBSTANCES UNDER NORMAL CONDITIONS OF USE AND UNDER FORESEEABLE ACCIDENT CONDITIONS

The main danger of products used in the warehouse is the danger of explosion. Explosivity of products is given by the combination of highly explosive substances (nitro-glycerine and penthrite), explosive substances (nitro glycol and trinitrotoluene) as well as oxidizing substances (ammonium nitrate or sodium nitrate). The presence of fuels (e.g. gas-oil in Nitramon) also makes a substance such as ammonium nitrate to become an explosive.

Explosives are unstable and can detonate in the event of strong shocks caused by kicks, frictions, an auxiliary detonator or a previous explosion. Basically, explosives are not flammable substances (they do not burn but explode), but if involved in a fire, the explosion is imminent. Explosion can also occur under high humidity conditions (including under water). Explosion produces a strong energy release (blow-out, shock wave) due to decomposition and ultra-fast combustion in simple products: oxide and carbon dioxide and nitrogen oxides. Combustion is possible even in the absence of air because of the oxygen produced in the decomposition process. Explosive gases are toxic but, due to their low quantity, they are not considered to be a major hazard to humans or the environment, especially if the explosion takes place in an open environment.

Although some explosives contain highly explosive substances that are difficult to control (such as nitro-glycerine), through blends that contain stabilizing and absorbent substances, this risk is greatly diminished, being low under strict compliance with safety precautions. A danger in this sense is that nitro-glycerine has the tendency to leave the absorber in time and to separate itself in the form of drops, phenomenon known as exudation. If this phenomenon occurs, the entire batch is declared inappropriate and will be destroyed.

Some explosives contain toxic substances: trinitrotoluene, or very toxic substances: nitro glycol and nitro-glycerine that may have adverse effects on employees. Due to the relatively low content of these substances, to packaging and, in particular, to safety measures for handling and use (because of the explosive nature), the toxicological risk is low. However, when handling and using explosives, especially when changing damaged packaging or recovering potential scattering, it should be borne in mind that some explosives contain toxic substances.

Some explosives contain ammonium nitrate which is a soluble substance which, when reaches soil, can dissolve in water, migrate and infest the groundwater.

DANGEROUS AREAS AND PROCESSES

Dangerous processes in explosives warehouses are those in which dangerous substances are permanently or temporarily present. Thus, the following processes can be considered as dangerous within the site:

- Storage of explosives in warehouses;
- Loading / unloading explosives;
- Ammonium nitrate storage;
- Loading / unloading ammonium nitrate;

The dangers within the site are caused by the presence of oil products. The hazard categories are as follows:

- Risk for fire and explosion;
- Risk for soil pollution in case of wastage;
- Risk for air pollution by combustion gases in case of fire;
- Risk for personnel in case of contact, prolonged exposure or ingestion;
- Risk for pollution by toxic gas decomposition: nitrogen oxides and ammonia.

Areas considered dangerous within the site are as follows:

- Explosive warehouses;
- Car loading / unloading ramp, only during operation;
- Ammonium nitrate storage room.

Following the analysis of risk factors from documents provided by the beneficiary and in-situ assessment of workplaces, the activities / workstations where conditions for potentially toxic / explosive / flammable atmospheres are present are handling and transport of hazardous chemicals and underground transportation galleries.

Another risk factor identified on the platform under study is the explosives warehouse. Even if it holds all the necessary permits / authorizations in accordance with current legislation and observes safety distances to adjacent targets it is considered as an explosion hazard because of stored and handled hazardous substances and products.

IMPACT OF EXPLOSIVES ON AIR

Massive blasting in quarries represents a source of air pollution, because a cloud containing dust and gas is formed during blasting, cloud that travels over larger or smaller distances, polluting the territory in the vicinity of the quarry.

The gas spreading distance depends on both their volume and the movement direction of air currents.

Each explosive is characterized by the release of a volume of gases into the atmosphere, gases represented by NO, NO_2, NO_3, NO_x, CO, CO_2, SO_2.

The environmental impact of quarry blasting is represented by:

- air pollution with dust and gases;
- discarding the material;
- creating an overpressure in the line of a shock air wave;
- producing a seismic effect;
- Strong noise pollution, determinable by vibration etc.

Also, performing quarry blasting leads to an undisciplined, rapid airborne emission of explosive products (dust and gases), characterized by a certain amount of energy, which develops a pressure wave represented by the air shock wave. This wave is characterized by an overpressure, with a sudden increase in pressure, over atmospheric pressure, causing vibrations of atmospheric air.

CONCLUSIONS

The issue of explosives use in engineering activities and of the quantification of explosions effects on environment has, over time, been the subject of numerous studies and researches designed to adopt technical norms or prescriptions to regulate this activity and, in particular, work technology.

In order to determine the measures to maintain the qualitative parameters of air, to protect the workers' health and to protect the environment of neighboring areas, the quantity of gases released by different types of explosives and of different diameters must be determined. Therefore, it is estimated that at the moment of detonation, the impact of this activity on air, generated by gas emissions from massive quarry blasting by using explosives for civil use, will be significant.

From the findings it can also be concluded that the results obtained clearly and objectively reflect the possibility of harming both employees detonating explosives and the environment, being characterized by dangerous values for their health and safety.

REFERENCES

1. Law 104/2011 on ambient air quality
2. Security report, SC MAXAM SA- Victoria workstation, Brașov County
3. Report of the environmental impact assessment study developed by INCD INSEMEX Petroşani
4. Eskikaya, S., Evergen, T., Bilgin, N. - Une methode non conventionelle sur l'efficacite de tir dans les mines de E.L.I. - The 16th World Mining Congress Sofia, Bulgaria, 1994
5. Emilian Ghicioi , George Artur Găman, Dan Gabor ,Nicolae Vlasin, Maria Prodan, Vlad Pasculescu, Dragoș Vasilescu - Prevention of accidental pollution with the combustion gases after the occurrence of explosions of air - gas by knowing of velocities for the front of flames and pressure waves, SESAM 2015
6. D.A. Kessler, V.N. Gamezo, E.S. Oran, Simulations of flame acceleration and deflagration-to-detonation transitions in methane–air system, Science Direct, Combustion and Flame Journal, 2010

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COLLECTION AND TREATMENT OF LEACHATE FROM LANDFILLS IN ORDER TO REDUCE POLLUTION LEVELS

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ABSTRACT

Human society has several major problems and the most acute is the unwanted consequences of environment pollution. The intense use of natural resources and the great amount of the generated waste tend to change the natural environment and its self adjusting reactions tend to affect life and the healthy ambient. The house wastes represent one of the best indicators who measures the economical vitality and the way of life of the society.

This paper deals with the problems of drain and processing the levigate from the non-ecological landfills.

Key words: environment, landfill, levigate, drain and processing technology, pollution level.

INTRODUCTION

Taking into account the limited degree of affordability of major environmental pollution and its effects certainly need to act with full responsibility for the promotion of environmental protection as part of the development of human society.

In recent decades the cheapest solution to the waste problem was that of storage. Currently there is no single accepted approach to waste management.

Under a non ecological landfill which doesn't have, sealing the base and side walls, drainage system and leachate collection, pools or places for storage and storage of liquid toxic or less toxic and / or dangerous, exploitation relevant activities taking place in a warehouse, the impact on the environment is significant.

Because most municipal landfills do not have a perfect foundation waterproofed, can occur leachate infiltration into soil, subsoil and groundwater pollution causing these environmental factors.

To this end the paper aims to present the problem of landfill leachate collection and treatment of municipal unchecked in order to reduce pollution levels by developing technologies and a model of collection and treatment of leachate from municipal waste deposits uncontrolled.

THE CURRENT ASPECTS REGARDING THE LANDFILLS

Due to harmonize national legislation with the European Union, some legislation was taken over.

The leachate collection methods presented in the current national legislation refers only to controlled landfills. There is currently no standard method for collecting leachate to reduce pollution of soil, subsoil and groundwater.

Under the legislation, leachate treatment can be performed in two types of systems, namely:

- Own treatment plant to allow discharge leachate deposit directly into receiving waters in compliance with legislation;
- Leachate pre-treatment plant for disposal in a waste water treatment plant city, with respect to effluent quality parameter values. In the case of uncontrolled deposits (mostly from Romania) there are facilities for the collection and treatment of leachate.

In this respect the uncontrolled municipal landfill where there is no collection facilities leachate treatment plants shall a collection and pretreatment technology for lower concentrations of salts, heavy metals and organic substances.

TECHNICAL CONSIDERATIONS ON LEACHATE

Without using water in the process of municipal landfills, wastewater resulting, so called leachate.

This results in a proportion of 20-30% of the waste deposited moisture gradients (in case domestic waste and of plant), the remaining 70-80% coming from:

- rainwater falling on ramp surface and percolating their way solubilizing and involving a variety of organic and inorganic compounds, depending on the nature of the waste;
- rainwater leaking from the slopes.

In conclusion leachate is produced as a result of leaching by rainwater waste and waste resulting from moisture - free leakage downstream - produced by infiltration, groundwater pollution, especially of the phreatic surface and surface water discharging.

The physico-chemical, spectrophotometric and gas chromatography were established main physico-chemical characteristics of leachate that will be shown below:

Table 1. The main physical-chemical characteristics of a medium leached

INDICATORS	VALUES	NATURE OF POLLUTION POLLUTION
pH	6,1	Acid
Total organic carbon	1700 mg/l	Organic pollution
CBO5	2500 mg/l	
Organic substances	5000 mg/l	
Na;K;	3000 mg/l	Mineral pollution
Ca;Mg;	2000 mg/l	
Cl;SO4;	5000 mg/l	
NH4	700 mg/l	
Total phosphorus	6 mg/l	
Fe	900 mg/l	Heavy metal and nonferrous pollution
Mn	25 mg/l	
Zn	10 mg/l	
Other metals such as: Co, Ni, Cu, Cr, Pb, Mo, As, Hg	10 mg/l	

Two important features are noted:

- CBO5/CCO report that characterize the organic aspect of a deposit to be of the order of 0.5 to young deposits, the ratio decreasing to zero for the old;
- If for a long time BOD5 can reach values close to zero, it will not CCO keep up with that can remain notable in the g / l.

PRESENTATION OF TECHNOLOGY FOR TREATMENT OF LEACHATE

The collector / drain uncontrolled leachate from municipal waste landfill will be achieved by lowering the hydrostatic groundwater if leachate contaminated groundwater by conducting drilling that leads to so-called cones of depression.

Water contaminated groundwater extracted from wells lexiviat using a submersible pump. Wells (which will extract water from polluted) grid will be made to determine the groundwater flow gradient. It will also establish a barrier cones depressive role wastewater drainage.

The waste water is extracted with submersible pump (Fig. 1) placed in an air-liquid which serves to dissolve air in the waste water.

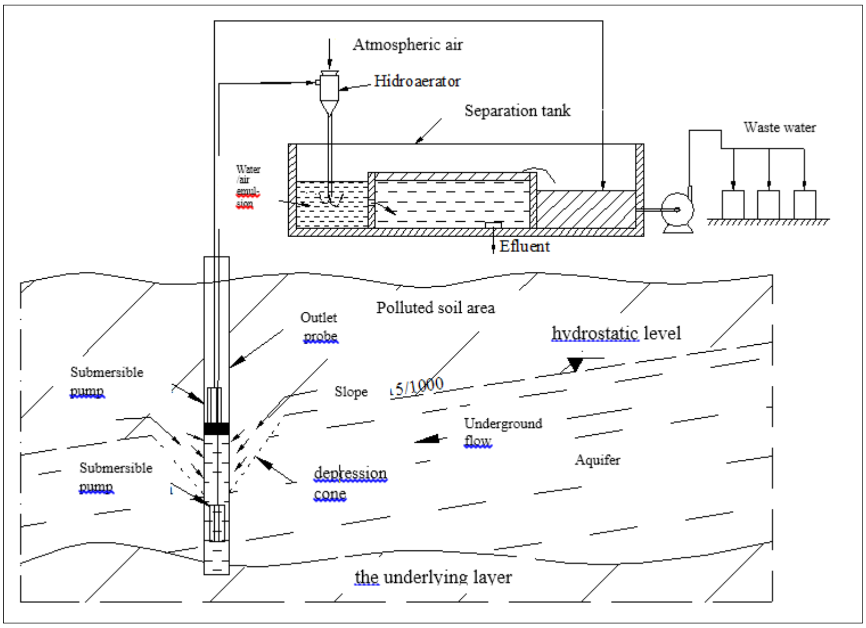

Figure 1. Flow Technology of drainage and wastewater contaminated a domestic landfill

By diluting the leachate to groundwater water which is obtained through a single physico-chemical treatment step can discharge sewage networks.

Hydro-airator is a static device that works on the principle of jet pump, with which to reduce chemical and biochemical oxygen content of the wastewater.

MEASURES OF INTEGRATION IN ECOSYSTEM OF THE WASTE DEPOSITS

Following the closure of municipal landfills redevelopment of the question of territorial space occupied by them. Such measures are necessary re-ecologisation some affected areas. There are three types of interventions for environmental recovery of the affected areas, the first type requires reconstructing the landscape as it was before degradation, the second type looking for a destination inventing new forms of re-use or attempt to satisfy the demands advanced community last type concerns accesses the affected areas provisional, pending final decisions taken by law enforcement.

To play the circuit ground surface storage capacity is exhausted by the following measures are recommended:

- Flatwork so as to create conditions for regeneration of soil fertility and plant culture or conditions for constructive arrangements. Leveling will be done with bulldozers and do both in the longitudinal and transverse.
- Topsoil filing works to biological recultivation. Given back to agricultural areas must be to a depth of 50 cm, a clay or sand-clay structure, with about 15% clay material capable to retain moisture and to have the water and air permeability as

well as a good capacity absorption rich in P, K, Ca, S, Mg without containing, dangerous substances.

- Drainage works in areas with slope of 2-3%, after placing topsoil on required thickness;
- Biological recultivation works as the rendering solution used in the economic cycle of land degradation. In the first 4-5 years after repository closure is good as shown in circuit areas to cultivate plants used as green manure and thereafter can proceed to achieve normal cultivation.

CONCLUSIONS

Human society faces a number of major problems, among which highlights the increasingly more negative consequences of environmental pollution. Waste is one of the best indicators that measure economic vitality and way of life of a society.

Currently, waste management and treatment have become complex and crucial issues for achieving sustainable development. Leachate is produced as a result of leaching by rainwater waste and waste resulting from moisture - free leakage downstream - produced by infiltration, groundwater pollution, especially of the phreatic surface and surface water discharging.

Following the closure of municipal landfills redevelopment of the question of territorial space occupied by them. Biological recultivation works are the most used solutions play in the economic circuit of degraded land areas.

REFERENCES

1. Ozanne,F., 1990, Les lixiviats de décharge, le point des connaissances en 1990. L'Eau: Techniques, Sciences et Méthodes juin 289-312;
2. Lorand T., Vlad P., 2016, Industrial and domestic wastewater treatment, Focus Publisher, Petroşani, ISBN 978-973-677-312-9;
3. Pişota, I., ş.a., 2005, Hydrology, University Publisher, Bucureşti;
4. Lorand T, Angelica Drăghici, Marius K., 2008, Negative effects of Valomir landfill, for the Uricani town on human health and environmental factors, Annals of West University of Timişoara. Series of Chemistry 17(3), ISSN 1224 – 9513
5. Kovacs M., Case study on waste landfill closure in the Municipality of Târnăveni, International Simposiun Health and Safety at Work, SESAM 2007
6. GD no. 1470 / 2004 National Strategy on Waste Management and the National Waste Management Plan;
7. GD no. 349 / 2005 concerning waste storage;
8. GD no. 1292/2010 amending and supplementing Government Decision no. 349/2005 on waste storage;
9. Order no. 757 of 26 November 2004 approving the Technical Norms concerning waste storage;
10. Order no. 95 of 12 February 2005 establishing the acceptance criteria and preliminary procedures for the acceptance of waste storage and the national list of waste accepted in each class of landfill

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ENERGY RECOVERY FROM HAZARDOUS WASTE IN REPUBLIC OF SERBIA – A REVIEW

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ABSTRACT

This paper presents energy recovery data by hazardous waste treatment in the Republic of Serbia (RS). Such waste treatment meets modern requirements of environmental protection, by reducing waste and increasing energy use from alternative sources. From a total of 210.000 tons of hazardous waste generated in the RS, only 4.300 tons is utilized as an energy source. Quantity and contribution data of hazardous waste fractions for energy recovery by its treatment in the RS in 2014, shows that only two categories of hazardous waste („waste containing oil“ and „oil from oil/water separator“) are treated in a satisfying manner, but in a small quantities.

Key words: hazardous waste, recycling, energy, incineration.

INTRODUCTION

According to available data, the European Union produces over two billion tons of waste per year, about 250 million tonnes are wastes from households and 90% of residual waste consists of industrial, commercial, agricultural and other wastes that are generated during some economic activity 1. On the other hand, rapid economic growth leads to an increase in energy consumption and reduction of raw materials used to generate final energy 2.

In modern society, the lack of resources has been dramatically increasing due to progress of civilization. Main sources of primary energy in the world till the year of 2014 were primarily fossil fuels 3. Consequences of their exploitation, being harmful to the environment and human health, took on a large scale. The way to overcome these problems is transition to an alternative energy sources.

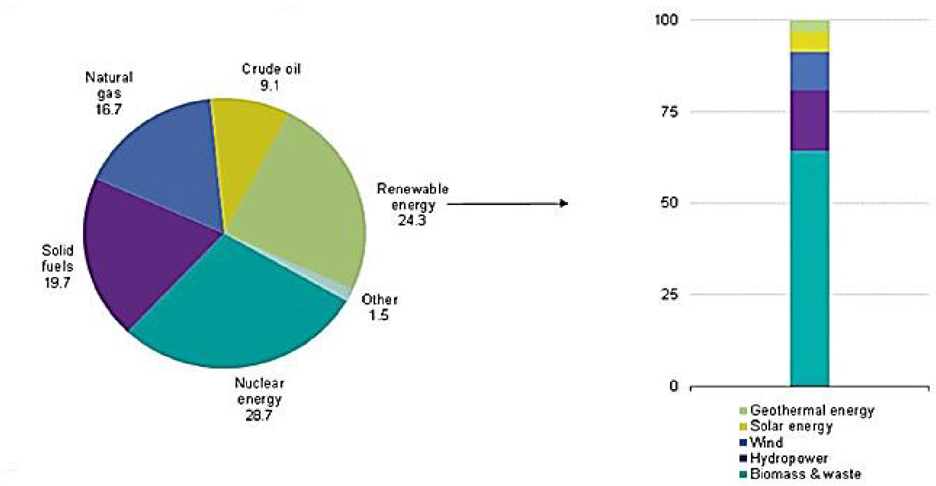


Figure 1. Primary energy sources in the world in 2013 3

The concept of sustainable development implies that environmental externalities generated by human activities must be reduced to a minimum. In fact, the definition of sustainability leads to a measurable upper limit for untreated or treated waste 1. It is, therefore, necessary to promote use of best techniques available and innovative solutions in the production processes, in order to reduce the depletion of the natural, finite resources and increasing quantity of waste. Today, the one of the most popular principles is so-called „3R" principle of sustainable development: reduced use of raw materials and harmful emissions (Reduce), repeated use of items (Reuse) and recycling of items which cannot be reused (Recycle) 4, as well as the term „circular economy", which considers more efficient use of raw materials and waste resulting from the use of a product. Generation of large amounts of waste and reduction of raw materials for final energy production could be partially solved by using the waste as an energy source.

European Union (EU) adopted in 2002 VI Action program for the Environment (Decision 1600/2002/EC) 5, main priorities of which are prevention and waste management. One of the primary objectives of this decision is separation of waste generated in the different economic activities, so that environmental damage caused by economic growth in the EU could be maximally reduced. New initiatives for the prevention of waste generation, better use of resources and more sustainable models of their use should greatly reduce the amount of waste generated. The EU approach to waste management is based on the principles of waste prevention as a key factor in all strategies for waste management, waste minimization and reduction of hazards to the environment and human health by reducing the presence of substances in products from which may later arise hazardous waste. In addition, recycling and use of waste with prior treatment of appropriate waste category can, also, significantly reduce its overall negative impact on the environment.

According to the international Agency for Environmental Protection (EPA), i.e. the EU Waste Framework Directive 2008/98/EC „Hazardous waste“ is defined as waste which has one or more hazardous properties specified in Annex III of this Directive [6-7]. Although the share of hazardous waste in the total amount of waste generated is low, the creation of this waste requires special attention because of the potential hazard to human health and the environment. Hazardous waste is generated in many industries. Generally, the sources of hazardous waste are industry, construction industry, health sector, trade and services, households and waste treatment sector.

One of possible and particularly attractive ways to reduce waste and reuse it is to generate heat. Many types of hazardous waste have a high thermal potential and can be used instead of conventional fossil fuels. The production of cement is especially suitable for waste reuse due to the application of high temperatures and long duration of burning phase in order to complete destruction of hazardous compounds. Based on Industrial Emissions Directive 2010/75/EU of the European Parliament, typical types of hazardous waste, which may be used for energy recovery include used solvents, residues from the refinery, sludge from the purification of industrial waste water, contaminated oils and halogen oils residues 8. There is the demand in EU market for waste oil as a fuel due to the large impact of energy prices on product prices. This is why, for example, European cement factories replaced fossil row material with fuels derived from waste, to the extent amounting even up to 75% of total primary energy demand [9-10]. The waste oils require a minimum pre-treatment, whereas the investment costs of secondary refining of oil are much higher 10.

USE OF HAZARDOUS WASTE AS FUEL

The most commonly used methods in which hazardous waste as an energy source is converted into some kind of final energy are incineration and pyrolysis.

Waste incineration involves the oxidation of combustible materials sufficient energy value contained in the waste. According to prescribed rules, waste incineration and co-incineration plants must be designed, constructed and equipped in such a way that the temperature of the exhaust gas reaches a temperature of at least 850°C 11. In the case of hazardous waste incineration which contains more than 1% of halogenated organic substances, it is necessary to attain a temperature of at least 1100°C 11. In addition, incineration plants must reach a level of combustion at which combustion residues of the total carbon content represent less than 3%, whereas their losses on ignition must be below 5% 11. Emission limit values, which are set out in Waste Framework Directive 2008/98/EC, must not be more than the limit values for exhaust emissions 6. It is also important to note that the incineration of municipal solid waste can be classified only as „reuse“, if the burning complies with the terms of energy efficiency that are established in the mentioned directive.

Problem is that residues from the incineration of hazardous waste are usually dangerous themselves. The ash remaining at the bottom, and fly ash residues after cleaning flue gas contains a high percentage of heavy metals and soluble salts, and therefore should be disposed in a hazardous waste landfill. However, extremely high temperatures, e.g. in rotary furnace, guarantee complete mineralization of waste and destruction of hazardous organic compounds 11.

These characteristics could be possessed by the both, non-hazardous and hazardous waste. However, required properties of secondary fuel that might be delivered from hazardous waste could be achieved by specified sorting, separating, mixing and processing in a preparatory stage of waste treatment.

In this case, the incineration of waste is applied to reduce amount of waste and reduce its impact on environment and human health, and is also used as an energy source. Incineration of waste is a key part of an integrated approach of waste management that enable the reduction, recycling and reuse of waste.

Pyrolysis is a process of thermal decomposition of a compound which occurs due to its long-term exposure to high temperatures in the absence of oxygen or other oxidizing agent. As a result of pyrolysis, complex chemical compounds included in composition of pyrolysed compounds decompose into simpler compounds. Mechanism of chemical changes that occur during pyrolysis process is very complex. Process is usually carried out at temperatures from 70 to 500° C, in order to prevent recombination reactions. Results of gas analysis shows that gas concentration of harmful gaseous substances after waste material pyrolysis is within the boundaries of the world's pollution emission standards 12. Increasing the reaction temperature leads to increase in portion of pyrolysis gas in relation to other reaction products, as well as to a reduction of solid and liquid phases. Pyrolysis gas is commonly used for recovery of energy, i. e. for heating or electricity generation.

ENERGY RECOVERY FROM HAZARDOUS WASTE IN RS

According to the Serbian Agency for Environmental Protection (SEPA), the total production of industrial and commercial waste in Serbia in the year of 2014 was 5,9 million tons, out of which 210.000 tonnes were classified as hazardous waste. For the participation of hazardous waste in municipal waste there is no data. Also, there are no relevant data for the hazardous waste production in the following years.

For the purpose of this study, data were collected from companies performing the collection, storage and treatment of hazardous waste in the RS. During 2014, only about 4,300 tons of total amount of hazardous waste were used for the purpose of obtaining the final energy and its utilization. Only two of three cement factories that exist in the RS have licence for incineration of hazardous waste, but only one uses this type of waste as an alternative fuel.

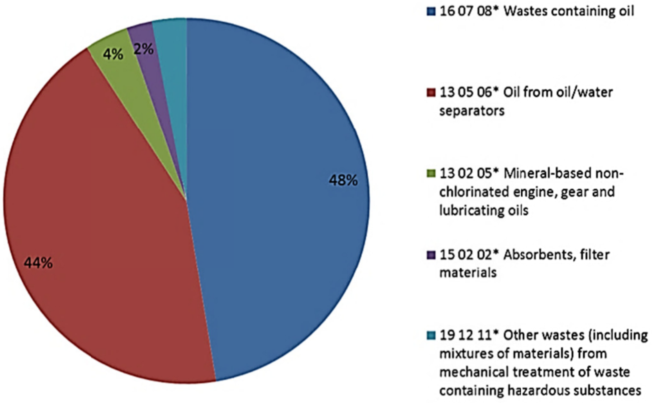
Table 1. shows amounts of hazardous waste used for recovery of thermal energy, classified according to the waste type.

Table 1. Quantities of hazardous waste used for energy recovery in Serbia in 2014

Waste code	**Waste type**	**Quantity used for energy recovery (t)**
12 01 07*	Mineral-based machining oils free of halogens (except emul-sions and solutions)	4
13 01 13*	Other hydraulic oils	1
13 02 05*	Mineral-based non-chlorinated engine, gear and lubricating oils	168
13 02 06*	Synthetic engine, gear and lubricating oils	1
13 02 08*	Other engine, gear and lubricating oils	16
13 03 10*	Other insulating and heat transmission oils	17
13 05 06*	Oil from oil/water separators	1.866
13 08 99*	Wastes not otherwise specified	27
15 01 10*	Packaging containing residues of or contaminated by hazard-ous substances	17
15 02 02*	Absorbents, filter materials (including oil filters not otherwise specified), wiping cloths, protective clothing contaminated by hazardous substances	100
16 01 07*	Oil filters	2
16 07 08*	Wastes containing oil	2.038
18 01 03*	Wastes whose collection and disposal is subject to special re-quirements in order to prevent infection	13
19 12 11*	Other wastes (including mixtures of materials) from mechanical treatment of waste containing hazardous substances	29
	TOTAL	**4.296**

From Table 1 it could be seen that types of waste marked 16 07 08* **i** 13 05 06*, i.e. „wastes containing oil" and „oil from oil/water separator" are responsible for the largest share in amount of hazardous waste used for recovery of energy, with 48 and 44%, respectively.

Figure 2. shows the most used types of waste in the total amount of hazardous waste used as a fuel in 2014 in the Republic of Serbia.



16 07 08* Wastes containing oil
13 05 06* Oil from oil/water separators
13 02 05* Mineral-based non-chlorinated engine, gear and lubricating oils
15 02 02* Absorbents, filter materials (including oil filters not otherwise specified), wiping cloths, protective clothing contaminated by hazardous substances
19 12 11* Other wastes (including mixtures of materials) from mechanical treatment of waste containing hazardous substances

Figure 2. The most common types of hazardous waste for reuse of energy in 2014 in RS

The Republic of Serbia currently does not have waste incineration plants, while co-incineration plants are found only in two cement factories. The best way to increase the number of such technological processes would be the stimulation of private investors in the construction of waste incineration plants, with fees to encourage the production of final energy from waste by raising the price per produced kilowatt hour (kWh).

However, the greatest difficulty for implementation of these new technologies in the RS represents negative public opinion regarding waste incineration, due to lack of adequate information on the social, medical and technical implications concerning incineration and disposal. Therefore, it is necessary to educate the population, popularization and promoting the use of best available technologies and environmentally friendly practices, with strict application of specially established emission limit values for installations covered by Directive 2008/1/EC on integrated prevention and control of pollution 13.

In the long term, investment and operating costs of the energy efficiency concerning waste incineration, as well as ecological benefits, represent a significant platform for use of this treatment of waste instead of dumping waste in landfills. The problems, particularly the ones inherent with disposal of hazardous waste, could, by this approach, effectively be reduced to a minimum for a longer period of time.

CONCLUSION

In 2014, only about 4,300 tons of hazardous waste, generated from the total quantity of 210,000 tons, were reused as fuel in the Republic of Serbia. The most used categories are „wastes containing oil“ and „oil from oil/water separator“, with 48 and 44%, respectively. Hazardous waste co-incineration is the only treatment in the RS in just one of three existing cement factories. In the RS there are no other facilities for incineration or pyrolysis processes. Although the use of waste oil is economically profitable and ecologically highly acceptable, the implementation of such projects is lacking for the time being, mostly due to the negative public opinion regarding the waste incineration, which is the issue that should be addressed through the adequate education on the implications of incineration and hazardous waste disposal. In the long run, according to the experiences of European countries, the investment and operating costs of energy recovery from waste incineration fully justify their purpose. Additionaly, the aspects of alternative energy sources utilization and reduction of waste amount, especially hazardous waste, are significant steps in bringing sustainable development principles closer together.

REFERENCES

1. Ruggiero, D. Waste in Europe: Production and Treatment of Waste in the European Union's Countries. *LT Economy*. Retrieved from [http://www.lteconomy.it/en/articles-en/articoli/waste-in-europe-production-and-treatment-of-waste-in-the-european-union-s-countries]. 2013.

2. Asafu-Adjaye, J. The relationship between energy consumption, energy prices and economic growth: time series evidence from Asian developing countries. *Energy Economics 22,* 615-625. 2000.
3. Eurostat, The statistical office of the Europian Union. Retrieved from [http://ec.europa.eu/eurostat/statistics-explained/index.php/File:Gross_inland_consumption,_EU-28,_1990%E2%80%932014_(%25_of_total_consumption)_YB16.png].
4. Qing-li, H. Theoretical Discussion on Precedence Sequence of 3R Principle about Circular Economy. *Environmental Protection Science 02*. 2006.
5. Decision No 1600/2002/EC of the European Parliament and of the Council. Retrieved from [http://eur-lex.europa.eu/legal content/EN/TXT/PDF/?uri=CELEX:32002D1600& qid=1494469684643&from=en].
6. Directive 2008/98/EC on waste (Waste Framework Directive). Retrieved from [http://ec.europa.eu/environment/waste/framework/].
7. Environmental Protection Agency (EPA). (2002). *European Waste Catalogue and Hazardous Waste List.* Environmental Protection Agency (EPA).
8. Directive 2010/75/EU of the European Parliament and of the Council. Retrieved from[http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32010L0075&from= EN].
9. Chatziaras, N., Psomopoulos, C. Use of waste derived fuels in cement industry: a review. Management of Environmental Quality: An International Journal, 27 Iss. 2, 178-193. 2015.
10. Chinyama, M. Alternative Fuels in Cement Manufacturing. InTech, Rijeka, Croatia. 2011.
11. Batterman S. Findings on an Assessment of Small-scale Incinerators for Health-care Waste. *Water, Sanitation and Health Protection of the Human Environment, 58.*
12. Nema, S.K., Ganeshprasad, K.S. (2002). Plasma pyrolysis of medical waste. *Current Science, Vol. 83,* 271–278. 2004.
13. Directive 2008/1/EC Integrated Pollution Prevention and Control Directive – new version. Retrieved from [http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri= CELEX:32008L0001:EN:NOT].

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PREVENTIVE EFFECT OF LIPOIC ACID DURING TOXIC EFFECTS LEAD OVER DNASE ACTIVITY

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ABSTRACT

In vitro studies in this study are used for testing the toxicity of heavy metal (Pb) and its mechanism of action at the molecular level on the structure of the enzymes (endonucleases) under controlled laboratory conditions. In this study was investigated toxic effect of heavy metal with purified enzymes DNase I and II, ie. alkaline and acidic DNase. In *in vitro* conditions, a lead salt lead to an increased activity of acidic and alkaline DNase. The results of these tests show that this can be prevented by adding the protector (alpha-lipoic acid).

Key words: Lead, alpha lipoic acid, *in vitro* experiment, DNase.

INTRODUCTION

Lead in nature appears as metallic lead, in the form of inorganic compounds and organometallic compounds. Average concentrations of lead in the soil are between 15 and 25 mg/kg [1]. In nature, is found predominantly in the form of sulphide, carbonate and mineral galena (PbS), cerussite and anglesite so that the soils of which are formed by decomposition of the mineral can contain a higher concentration of lead. Lead contamination is the "disease" of the environment because of its solubility, mobility, and accumulation in the soil [2]. Lead from drinking water is likely to absorb more than lead from food. According to some studies, adults absorb 35% to 50% of the entrained metal, and percentage of the absorbance for the children can be greater than 50%. On the absorption of lead beside growth affects the general physiological condition of the body [3].

Lead as a pollutant can be detected in all phases of the environment and biological systems. Since ancient times was known toxic effects of lead in living and working environment. Because of its presence in the environment, lead poisoning still remains a significant health problem in the world [4]. Especially inhabitants of large cities are increasingly exposed to the damaging effects of this metal, which today represents a main ecological problem. Acute lead poisoning in the working environment becomes an important issue to improve working conditions and protect people from exposure to sources of this metal [5]. The main routes of entry of lead in the body are the respiratory tract, through the skin and digestive tract [6]. Colors made from lead in 90% of cases are the causes of poisoning in children who play with toys painted these colors [7].

Symptoms of acute lead poisoning are abdominal pain, nausea, loss of appetite, fatigue, lack of concentration, insomnia, hallucinations, dizziness, headache, mood swings, arthritis. Death in cases of acute poisoning of people can occur at the input 25 to 30 g of soluble lead salt. Chronical exposure to these heavy metal leads to mental retardation, psychosis, hyperactivity, weight loss and muscle weakness and paralysis. The increased presence of this metal has been attributed to, in some cases, appearance of hypertension, cardiac arrhythmias, malignant changes in the digestive tract, lung, kidney [8].

Neurotropic operation of lead is also demonstrated on the central nervous system, what is known as lead encephalopathy or lead neuropathy. Long-term exposure of lead leads to reversible nephrotoxic effects such as chronic renal failure, which may later lead to gout.

Lipoic acid in a pure state has an unpleasant smell and taste. It manifests great activity in very small quantities. The effect of alpha lipoic acid is reflected in the intensification of the synthesis of ATP [9], she is participating in the assimilation of lactic acid, activating enzymes of cycle tricarboxylic acids, stimulating the growth of bacteria of lactic acid fermentation by replacing acetate (transfer factor acetate), stimulates the synthesis of CoA (utilization of fatty acids), can prevent liver damage by various toxins, normalize level of aldolase and transferase.

Alpha lipoic acid (ALA) is the most efficient known antioxidants for their lipo and hydrosolubility which allows the easy penetration into the cytoplasm, where she participate in the protection against free radicals, reactive, energy metabolism, regulation of gene expression, and so on. In the body, ALA can exist intracellularly, extracellularly and on membranes. Alpha lipoic acid is an antioxidant that is a relatively widely used. It is used in the treatment of many diseases [10]. Supplementation with lipoic acid, which can act as an antioxidant and reduce oxidative stress in a cell, has been observed in *in vitro* and *in vivo* studies [11].

Numerous studies tell about the biological relevance of application of lipoic acid in the cases of oxidative stress, or the differences between the antioxidant activity of lipoic acid and its derivatives [12,13]. Also, there are some studies about the spectroscopic and chromatographic analysis of structural and quantitative aspects of lipoic acid and its derivatives in a solution [14,15]. There are literature data on the application of lipoic acid and its derivatives as a chelator of heavy metals.

MATERIALS AND METHODS

The advantages of *in vitro* investigations are feasibility and reproducibility of the performance of pre-clinical trials, to thereby examine proteomics, effect on the structure of the enzyme, as well as the fact that it is clear from the enzyme so that it is avoided the effect of the other metabolites interact with the enzyme.

The disadvantages of *in vitro* tests are that these tests are prediction of the *in vivo* tests and that they can not reverberate the situation *in vivo*, as well as that there are no other enzymes involved in homeostasis like in *in vivo* assays so that there is no quantitative evaluation.

In *in vitro* assays are used purified enzymes, in this study these are DNase I and II, alkaline and acid DNase as commercial pure enzymes. For determining the activity of alkaline and acid DNase *in vitro* was used clean commercial enzyme by producer Sigma-Aldrich. Pre-incubation was performed with an enzyme and an appropriate buffer and were added heavy metals, or supplement, or combination there of (metal+supplement). Measurements were done on a spectrophotometer Beckman DU 530 (λ_{max} = 260 nm). The enzyme activity was expressed in international units per gram of protein (U/g protein).

STATISTICAL ANALYSIS

All the measurement results are shown as mean ± SD. For statistical results processing was applied Student's t-test for independent samples (Microsoft Office Excel). The results of this analysis are shown in tables and graphs (histogram).

RESULTS AND DISCUSSION

The presence of free radicals in biological materials was discovered a little more than 50 years. The free radicals can react with each other or with other less reactive species which causes a number of chain reactions. They are constantly forming in small amounts in the cells during physiological processes as a "by-products" of metabolism (oxidative phosphorylation in mitochondria, the oxido-reduction processes in the presence of metals of variable valence, in the process of metabolism of ethanol, in the synthesis of eicosanoids, in the process of lipid peroxidation of unsaturated fatty acids and during radiation). Toxic effects of free radicals can be divided into three groups: a) displacement of intracellular redox potential, b) oxidative modification of lipids, proteins and DNA and c) activation of gens.

Oxidative stress is caused by increased production of reactive oxygen species (Parkinson's and Alzheimer's disease) [16], or a reduced ability of cells to neutralize it, through its internal antioxidants (e.g., mutation in the gene for superoxide dismutase in amyotrophic lateral sclerosis). Oxidative damage to DNA, leading to: interrupting the chain of a DNA, interactions bases within one coils, interaction base between two different coils, modified bases, loss of a base, modifications in a base, the creation of pyrimidine dimer, formation of photoproducts, creating obstacles in the DNA, interactions with proteins, the interaction with lipid peroxides (MDA) or deoxyribose oxidative modification, which leads to pathological change and the onset of the disease.

DNA repair mechanisms are: a direct reversal, repairation by cutting and recombination. The most important enzymes involved in DNA repair are: DNA endonucleases, AP endonuclease, pyrimidine-hydrate-DNA glycosylase, DNA polymerase, β-lyase, δ-lyase, Dezoksifosfodiesterase, DNA ligase, etc. [17]. DNase are suitable enzymes for the removal of genomic DNA from cells. DNAses is referred as the executioners of apoptosis main responsible for the internucleosomal fragmentation of DNA from the cells in apoptosis. Internucleosomal DNA fragmentation, as well as biochemical marker of apoptosis, the chromosomal DNA in the interpretation of the fragment sizes oligonucleosomes [18].

Up to now it was found that deoxyribonuclease I (DNase I), the most famous of Ca / Mg-dependent endonucleases at the optimum pH of 7.4 that produces 3`OH DNA ends is involved in DNA fragmentation in the course of cell death [19,20]. DNase II (EC 3.1.22.1, deoxyribonuclease 3'-oligonucleotide hydrolases) in an acidic medium produces 3'-oligonucleotides. This is one of the earliest identified nuclease [21].

During the evolutionary development of the organism has been established a specific defense system of the potential harmful effects of free radicals, which is characterized as the antioxidant system. According to the nature and mode of action, antioxidants can be divided into: enzymatic (superoksiddizmutase, catalase, glutathione reductase, glutathione-S-transferase, etc.) and non-enzymatic (glutathione, vitamins A, C and E, albumins, ceruloplasmin, transferrin, bilirubin, uric acid, etc.) [22].

In *in vitro* conditions, the lead leads to an increase activation in alkaline and acidic DNase thus resulting in the formation of free radicals and oxidative stress. The results of these tests show that this can prevent by the addition of protector (alpha lipoic acid) (Table 1 and 2).

From the obtained results it is obvious that the lead significantly increase the level of alkaline DNase (15.80 ± 2.30 to 31.89 ± 6.04), and also the acid of the DNase I (10.01 ± 4,83 to 25.49 ± 6.31) compared to the activity of alkaline and acidic DNase in the control group. Alkaline and acidic DNase when supplementation of ALA after intoxication lead are reduced; for alkaline DNase (31.89 ± 6.04 to 20.90 ± 6.67), and for the acidic DNase (25.49 ± 6.31 to 21,41 ± 4.68) in relation to the group in which only the metal is added, ie. lead.

Table 1. Activity alkaline DNase in in vitro

In vitro	**Alkaline DNase**
	Average ± Stdev
Control	15,80 ± 2,30
Pb	31,89 ± 6,04
Pb + ALA	20,90 ± 6,67
ALA	10,20 ± 2,40

Table 2. Acid activity of the DNase in in vitro

In vitro	**Acid DNase**
	Average ± Stdev
Control	10,01 ± 4,83
Pb	25,49 ± 6,31
Pb + ALA	21,41 ± 4,68
ALA	8,61 ± 3,34

Probably this reduction of endonuclease activities in this model system is due to ALA as an antioxidant substance that seeks to reduce the negative effect of toxic metals, ie. lead [23]. From the results shown in Table 1,2 can be concluded that the effect of lead leads to cause increased oxidative stress, which is manifested by a significant increase in activity of the DNases in regards to the control group, which was without the addition of lead.

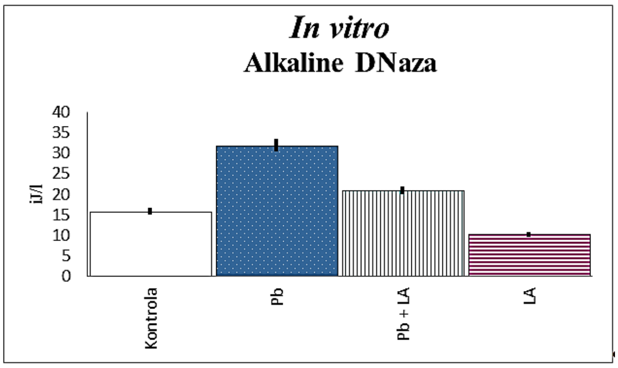

Figure 1. Alkaline Dnase activity while adding lead, as well as with and without supplement (ALA)

Numerous studies have shown that lipoic acid is a natural antioxidant, which serves as scavenger of free radicals. Literature data are mainly related to the effects of ALA at rehabilitation nitrosative stress in diabetes, nephropathy and coronary artery disease [24].

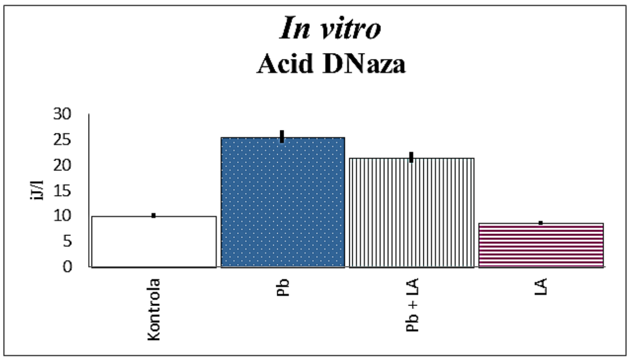

Figure 2. Acid DNase activity while adding lead, as well as with and without supplement (ALA)

Antioxidant (alpha-lipoic acid) can reduce the negative effects of heavy metal (Pb) because probably forms a stable self-associate them with a type of the complex, thus leading to a decrease in activity of alkaline and acidic DNase.

CONCLUSION

At the molecular level, the effect of lead is reflected in the increased production of reactive oxygen species. It is assumed that alpha-lipoic acid forms stable chelate complexes with Pb^{2+}, and that removes heavy metal and thus act as a good supplement and antioxidant to combat the toxicity of lead.

ALA can be thiol-chelator and potential choice in the treatment of lead poisoning. It is a preferred supplement because of the presence of -SH group which has the ability of complexing with heavy metals by an S-donor atom. ALA represents a significant source of antioxidants and therefore can recommend its application in the human diet, as a food supplement because its protective role is reflected in the prevention formation of free radicals.

Acknowledgments

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REFERENCES

1. Radojević, M., Bashkin, V. *Practical Environmental Analysis, Royal Society of Chemistry,* Cambridge, 1999.
2. Goyer, R.A. Toxic and essential metal interactions, *Annu. Rev. Nutr.* 17:37-50, 1997.
3. Flora, S.J.S., Flora, G.J.S., Saxena, G. Environmental occurrence, health effects and management of lead poisoning. In: Cascas S.B., Sordo J. (eds). *Lead: Chemistry, Analytical Aspects, Environmental Impacts and Health Effects*, Elsevier Publication, Netherlands, 158-228, 2006.
4. Goyer, R.A. Results of lead research: prenatal exposure and neurological consequences. *Environ Health Perspect*. 104(10):1050-1054, 1996.
5. Tong, S., McMichael, AJ. The magnitude, persistence and public health significance of cognitive effects of environmental lead exposure in childhood. *J. Environ. Med*. 1:103-110, 1999.
6. Fischbein, A. Occupational and environmental lead exposure. In WN. Rom (Ed.) *Environmental and Occupational Medicine*, Boston, Little Brown, 2:735-758, 1992.
7. Glotzer, D.E. Management of childhood lead poisoning: strategies for chelation. *Pediatr. Ann*. 23(11): 606-615, 1994.
8. Counis, M.F. L-DNase II, a Molecule That Links Proteases and Endonucleases in Apoptosis, Derives from the Ubiquitous Serpin Leukocyte Elastase Inhibitor. *Mol. Cell Biol*. 18:3612-3619, 1998.
9. Harris, RA., Joshi, M., Jeoung, NH., Obayashi, M. Overview of the molecular and biochemical basis of branched-chain amino acid catabolism. *J. Nutr*. 135(6):1527S-1530S, 2005.

10. Ziegler, D., Hanefeld, M., Ruhnau, K.J., Meissner, H.P., Lobisch, M., Schütte, K., Gries, F.A. Treatment of symptomatic diabetic peripheral neuropathy with the antioxidant alpha-lipoic acid. *Diabetologia,* 38(12):1425-1433, 1995.
11. Suzuki, Y. J., Tsuchiya, M., and Packer, L. Thioctic acid and dihydrolipoic acid are novel antioxidants which interact with reactive oxygen species. *Free Radical Res. Commun.* 15:255-263, 1991.
12. Arivazhagan, P., Thilakavathy, T., Ramanathan, K., Kumaran, S., Panneerselvam, C. Effect of DL-α-lipoic acid on the status of lipid peroxidation and protein oxidation in various brain regions of aged rats. *The Journal of Nutritional Biochemistry.* 13:619–624, 2002.
13. Matsugo, S., Yan, L.J., Konishi, T., Youn, H.D., Lodge, J.K., Ulrich, H., Packer, L. The lipoic acid analogue 1,2-diselenolane-3-pentanoic acid protects human low density lipoprotein against oxidative modification mediated by copper ion. *Biochemical and Biophysical Research Communications.* 240:819-824, 1996.
14. Chen, J., Jiang, W., Cai, J., Tao, W., Gao, X. and Jiang, X. Quantification of lipoic acid in plasma by high-performance liquid chromatography-electrospray ionization mass spectrometry. *Journal of Chromatography B. Analyt. Technol. Biomed. Life Sci.* 824:249-257, 2005.
15. Schepkin, V., Kawabata, T., Tritschler, H.J., Packer, L., 2D NMR of the metabolic antioxidant dihydrolipoic acid and its derivatives. *Free Radical Research.* 25:195-205, 1996.
16. Valko, M., Leibfritz, D., Moncol, J., Cronin, M. T. D., Mazur, M., Telser, J. Free radicals and antioxidants in normal physiological functions and human disease, *International Journal of Biochemistry and Cell Biology,* 39(1):44–84, 2007.
17. Birnboim, H. C., DNA strand breakage in human leukocytes exposed to a tumor promotor, phorbol myristate acetata, *Science.* 215:1247-1249, 1982.
18. Wyllie, AH. Glucocorticoid induced thymocyte apoptosis is associated with endogenous endonuclease activation. *Nature.* 284:555-556, 1980.
19. Lacks, SA. Deoxyribonuclease I in mammalian tissues. Specificity of inhibition by actin. *J. Biol. Chem.* 256(6):2644–2648, 1981.
20. Polzar, B., Peitsch, MC., Loos, R., Tschopp, J., Mannherz, HG. Overexpression of deoxyribonuclease I (DNase I) transfected into COS-cells: its distribution during apoptotic cell death. *Eur. J. Cell Biol.* 62(2):397-405, 1993.
21. Catcheside, DG., Holmes, B. The action of enzymes on chromosomes. *Symp. Soc. Exp. Biol.* 1:225–231, 1947.
22. Đorđević, V., Pavlović, D., Kocić, G. *Biochemistry of free radicals*, Niš, Sirius Print, (1):2000.
23. Nikolić, R., Jovanović, J., Kocić, G., Cvetković, T., Stojanović, S., Anđelković, T., Krstić, N. Praćenje efekata izloženosti olovu i kadmijumu u radnoj i životnoj sredini preko parametara standardne biohemijske analize krvi i aktivnosti endonukleaza jetre. *Hem. Ind.* 65(4):403-409, 2011.
24. Gaurav, D., Preet S., Dua, KK. Chronic cadmium toxicity in rats: treatment with combined administration of vitamins, amino acids, antioxidants and essential metals. *J. Food Drug Anal.* 18(6):464-470, 2010.

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ANTIOXIDANT ROLE OF GLUTATHIONE DURING ACUTE INTOXICATION BY CADMIUM

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ABSTRACT

In this study, it was performed *in vitro* testing effect of the toxic metals (cadmium) and the protective function of supplements -S donor ligand, glutathione, on the activity of alkaline and acidic DNase. For determining the activity of alkaline and acidic DNase clean commercial enzymes were used for determining the activity of alkaline and acidic DNase *in vitro*. Measurements were performed on a Beckman DU 530 spectrophotometer. GSH as a supplement (soft Lewiss's base) interacts with a metal ion, a soft Lewiss's acid. On this way, glutathione almost completely eliminates the metal toxic effects on the activity of endonucleases.

Key words: Antioxidant, glutathione, cadmium, DNase.

INTRODUCTION

Heavy metals are found naturally in the soil in certain concentrations. Heavy metals are often found in surface horizons of soil, which are not geochemical but the anthropogenic origin, actually, they arrived in the soil as a result of various human activities (industry, the application of agrochemicals, atmospheric depositions, etc.), which as a result can have a long-lasting contamination of soil and groundwater. The water may be constructed barely soluble carbonates, sulfates, and sulfides which are precipitated on the bottom of the water surface, where they accumulate. Animals and humans come into contact with heavy metals through food, water and air. In normal circumstances, there are three ways of entry of heavy metals in the body: through the skin, the gastrointestinal tract and through the respiratory tract. The heavy metals that are important for the prooxidant effect include: cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As), chromium (Cr), nickel (Ni), aluminum and biometali, such as copper (Cu), iron (Fe), zinc (Zn), manganese (Mn), cobalt (Co), and selenium (Se).

Cadmium is a widespread metal in nature and toxic industrial pollutant with expressed mobility. It is characterized as one of the 126 biggest polluters of the Agency for Environmental Protection USA. According to geochemical characteristics, cadmium is found in nature, together with zinc, copper and lead. Every year we produce about 13,000 tones of heavy metal [1]. According geochemical classification of chemical elements cadmium is lythophile and chalcophile element. Cadmium is replenished in the form of vapors and dust particles as oxide, chloride, fluoride, sulfide, carbonate, and acetate. Absorption takes place mainly through respiratory route, a small part of the gastrointestinal tract, and the transcutaneous way is insignificant. Systemic exposure to the influence of Cd leads to increased excretion of calcium and bone damage, as well as the change of activity of numerous enzymes. Resorbed cadmium is transported by the blood attached to a protein, metallothionein, and red blood cells. It is deposited mainly in the kidney, liver and pancreas. Cadmium excretion is slow. Symptoms of acute exposure to cadmium are nausea, vomiting, loss of smell, taste and appetite, abdominal pain [2]. Acute cadmium poisoning in laboratory animals causes damage to the liver and the testes, while chronic exposure leads to renal failure, anemia, immune disorders and bone lesions [3,4,5]. In contrast to acute chronic intoxication in humans leads to the development of some diseases, such as: chronic obstructive pulmonary disease, kidney disease (nephrotoxicity) and bones (arthritis, osteoporosis), anemia, growth disorder and other [6].

The antioxidant is any substance that is presented in lower concentration in relation to the substances which are oxidized, may prevent or substantially minimize their oxidation. This system is aimed at preventing the formation of free radicals, their removal or stop chain reactions. According to the nature and mode of action of antioxidants, they can be divided into: enzyme (superoksid dismutaza, catalase, glutathione reductase, glutathione-S-transferase, etc.) and non-enzymatic (glutathione, vitamins A, C and E, albumin, ceruloplasmin, transferrin, bilirubin, uric acid, etc.) [7]. While there is a balance between the production of free radicals and antioxidant protection of cells by free radicals, there aren't signs of a detrimental effect.

Glutathione (GSH) is a tripeptide of L-γ-glutamyl-L-glycine-cistenil which accounts for 90% of the total sulphide nonproteinaceous compounds cells and is an essential cofactor for some enzymes (glutathione peroxidase, glutathione S-transferase, glutathione, a transhydrogenase, glutathione reductase). The red blood cells are a kind of transport system for a glutathione and conjugates [8].

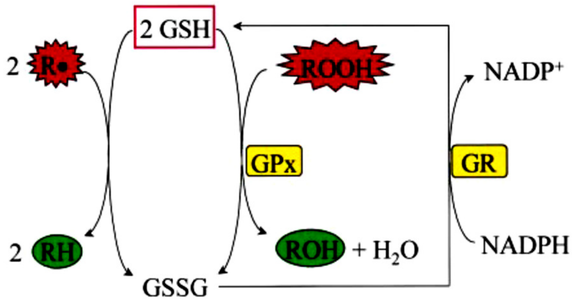

Figure 1. Schematic representation functions GSH as an antioxidant

Glutathione can be found in the cells as a participant in the metabolism, and protection of the transport in the cell. It is involved in the reduction of disulfide and other molecules, as well as conjugation with the compounds of the exogenous and endogenous origin. In this way it protects cells from the damaging effects of free oxygen radicals. Antioxidant role of glutathione reflected in slowing the aging process, atherogenesis, mutagenesis and carcinogenesis. Glutathione participates in other metabolic functions of cells, such as: the reduction and isomerization of disulfide bonds in structural and functional proteins, maintenance of the redox buffer system cells, leukotriene and prostaglandin synthesis, the synthesis of cysteine, to maintain the integrity of the cell membrane (the active transport of the substrate and ion homeostasis Ca^{2+}, stabilization of the receptor, cytoskeletal activity), amino acid transport across the cell membrane (tubules, of the mucous membranes of the small intestine and brain chorionic plexuses) [9].

MATERIALS AND METHODS

In vitro assays are a group of pre-clinical tests with the *in vivo* tests in animals, which is preceded by *in vivo* studies in man ie. clinical trials. *In vitro* studies of a substitute of animal models and are clear guideline for pre-clinical studies in animals. In *in vitro* assays using a purified enzyme, in this study to have DNase I and II and the acidic DNase as commercial pure enzymes.

For determining the activity of alkaline and acid *in vitro* DNase was used to clean commercial enzyme manufacturer Sigma-Aldrich. Pre-incubation was performed with an enzyme and an appropriate buffer and added to the heavy metals, or supplement, or any combination thereof (metal+supplement). The incubation was carried out at 37°C for 2h [10]. Measurements were done on a spectrophotometer Beckman DU 530 (λmax=260 nm).

STATISTICAL ANALYSIS

For statistical results processing was applied Student's t-test for independent samples (Microsoft Office Excel). Statistically, significant results are shown as $p < 0.01$; $p < 0.05$ and $p < 0.1$. The results of this analysis are shown in tables and graphs (bar graph).

RESULTS AND DISCUSSION

Free radicals are atoms, ions, or molecules with one or more unpaired electrons in their structure, which make them very unstable and reactive [11]. In reactions with other biomolecules for example, proteins, lipids and nucleic acids, there are changes in the structure and function of these compounds so as to produce damage and death of the cell [12,13]. Antioxidant system allows the elimination of free radicals from the body. Reactive oxygen play a key role in the pathogenesis of aging and aging-related diseases [14]. A DNA molecule represents a chemical basis of inheritance in prokaryotic and eukaryotic cells. Changes in the structure of DNA lead to mutations of genetic defects, carcinogenesis, or apoptosis (programmed cell death).

Oxidative modification of DNA can cause different agents. One of these metals with variable valence is involved in the creation of hydroxyl radicals.

The enzymes responsible for the internucleosomal cleavage of DNA or RNA molecules in apoptosis are the endonuclease. Endonuclease catalyze the breakdown of inter-nucleotide bond at the same time at multiple locations within the nucleic acid molecule [15]. Depending on the nucleic acid, according to which exhibit specific activity, these enzymes are divided into: deoxyribonuclease (desoxyribonuclease, DNase EC 3.1.4.5), which exhibit specific activity to the DNA and ribonucleases (ribonuclease, RNase-free, EC 2.7.7.16), which act on the RNA.

Desoxyribonuclease I (DNase I) are enzymes which hydrolyze the desoxyribonucleic acid. Internucleosomal DNA fragmentation, as well as biochemical marker of apoptosis, the chromosomal DNA in the interpretation of the fragment sizes oligonucleosomes [16].

Since:

- deoxyribonuclease I (DNase I called that. Alkaline DNase) and
- deoxyribonuclease II (DNase II, ie. an acid DNase).

One of the aims of this study was to examine the *in vitro* effect of cadmium, as well as the effect of the substance thiol, -S donor ligand (GSH) independently or as a supplement, to the activity of commercial enzymes DNase. *In vitro* examinations in this study are used for testing the toxicity of heavy metals (Cd) and its mechanism of actions at the molecular level in the structure of the enzymes (endonucleases) under controlled laboratory conditions. In *in vitro* assays in this study with purified enzymes DNase I and II, ie. alkaline and acidic DNase was investigated genotoxic and cytotoxic effect of cadmium in the cases where the toxic substances disturb the homeostasis of the biochemical processes in the cell and is not recommended and warranted is administered *in vivo*. This test can be repeated and justifiably used as preliminary research which is basis for further preclinical and clinical research. Due to the inability to achieve a complex system, it is impossible to estimate the impact of all factors on the activity of the enzyme and the answer to the question whether the desired effect occur in living organisms. In this study, this type of research is the basis for further *in vivo* studies in which they will be given a comprehensive insight in animal models. In this way, in the *in vitro* assays studying the proteomics (effect of metal on the structure of the enzyme), and not in genomics is the case of *in vivo* tests.

The measurement results of alkaline and acid of the DNase I because of the effects of cadmium, as well as the tread (glutathione) are given in Table 1 and 2, and histograms 1 and 2.

Table 1. Activity alkaline DNase in in vitro

In vitro	**Alkaline DNase**
	Average ± St dev
Control	15,80 ± 2,30
Cd	39,42 ± 3,25
Cd + GSH	20,9 ± 6,07
GSH	13,24 ± 8,73

Table 2. Acid activity of the DNase in in vitro

In vitro	**Acid DNase**
	Average ± St dev
Control	10,01 ± 4,83
Cd	32,50 ± 8,66
Cd + GSH	16,89 ± 3,34
GSH	8,99 ± 5,31

In *in vitro* assays cadmium indirectly exerts influence to be genotoxic. Literature data indicate that the cadmium in the *in vitro* studies suppresses the enzyme in the lungs of rabbits [17]. It has been shown that the cadmium exhibits an inhibitory effect on the activity of many enzymes (eg. P5Npirimidin-5'-nucleotidase (P5N, E.C. 3.1.3.5)), however, when the metal is added to a substance in a preincubation for example metallothionein inhibitory effects of metals on the activity of the enzyme (P5N) substantially reduces [18]. In this study, the cadmium is increasing the activity of alkaline and acidic DNase in *in vitro* conditions.

Acording to the results of these studies (Table 1, 2), glutathione, as a component of the antioxidant and as a metal-chelating agent, manifests protective function. Glutathione reduces cytotoxicity in the *in vitro* system that is caused by effect of cadmium.

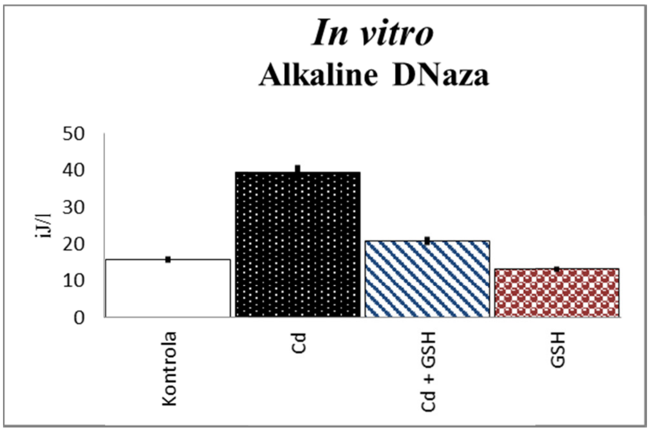

Figure 1. Alkaline DNase activity while adding cadmium, as well as with and without supplement (GSH)

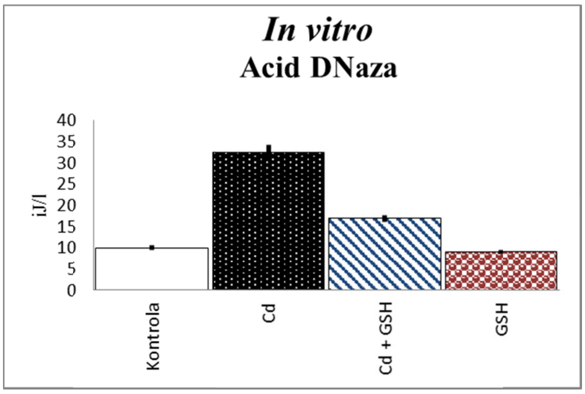

Figure 2. Acid DNase activity while adding cadmium, as well as with and without supplement (GSH)

According to the results of these tests (Histograms 1, 2), it is registered a positive effect of the substance thiol, -S donor ligand (GSH) and the activity of the DNase (I and II) intoxication with a toxic metal cadmium. In the *in vitro* studies the impact of the environmental factors and the effect of the individual metabolites to the enzyme's activity is eliminated. Because of this, the effect on the genetical level, possibility of genetical expression and enzyme modification of the base are eliminated, too.

CONCLUSION

In vitro studies have shown that an indirect effect of cadmium leads to the production of free radicals and oxidative stress. There is no medical chelating method which is fully effective for the treatment of cadmium toxicity. In this *in vitro* study, it was observed that the treatment for the removal of heavy metals from the so-called human organism chelation therapy is based on the coordination ability of the metal ions on the one hand and to hold the donor atom bioligands (-O, -N, -S) across which a stable form of associations type of complex is thus significantly reducing the toxic effect of cadmium. Good chelator is glutathione as an antioxidant which bind cadmium, and thereby increases the protection from oxidative stress. It is known that chelators, and antioxidants such as glutathione protect against potential adverse effects of reactive oxygen species.

Acknowledgments

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REFERENCES

1. Valko, M., Morris, H., Cronin, M.T.D. Metals, Toxicity and Oxidative Stress. *Current Medicinal Chemistry*. 12:1161-1208, 2005.

2. Wentz, P.W. Chelation Therapy: Conventional Treatments. Burlington, In: Advance Magazines, Administrators of the Laboratory, *Lab. Corp*. Burlington, NC, King of Prussia, PA, Merion, 2000.
3. Goering, P.L., Waalkes, M.P., Klaassen, C.D. Toxicology of cadmium, In: Goyer, RA., Cherian, MG., editors, *Toxicology of metals: Biochemical aspects Handbook of Experimental Pharmacology*, Springer; New York, NY, USA, 115:189-213, 1995.
4. Waalkes, M.P., Cadmium carcinogenesis in review. *J. Inorg. Biochem.* 79 241-244, 2000.
5. Klaassen, C.D., Liu J., Choudhuri, S. Metallothionein: An intracellular protein to protect against cadmium toxicity. *Annu. Rev. Pharmacol. Toxicol.* 39:267–294, 1999.
6. ATSDR, Agency for Toxic Substances and Disease Registry.Toxicological profile for ATSDR. Toxicological profile for cadmium. Atlanta, GA. *Agency for Toxic Substances and Disease Registry*, 1999.
7. Đorđević, V., Pavlović, D., Kocić, G. *Biochemistry of free radicals*, Niš, Sirius Print, (1), 2000.
8. Jovanović, J., Nikolić, R., Kocić, G., Glutathione protects liver and kidney tissue from cadmium- and lead- provoked lipid peroxidation. *J. Serb. Chem. Soc.* 78(2):197-207, 2013.
9. Wendel, A., Feurstein S. Drug-induced lipid peroxidation in mice. I. Modulation by monooxygenase activity, glutathione and selenium status. *Biochem. Pharmacol.* 30:2513-2520, 1981.
10. Kocić, G., Pavlović, D., Đorđević, V., Bjelaković, G., Stojanović, I. Role of nitric oxide and peroxynitrite in apoptosis–relation to endonuclease activity. *Jugoslov. Med. Biohem.* 22(2):93-100, 2003.
11. Halliwell, B. Reactive oxygen species in living system, Source, biochemistry and role in humane disease. *Am. J. Med.* 91:14-21, 1991.
12. Freidovich, I. Fundamental aspects of reactive oxygen species, or what's the matter with oxygen? Ann NY. *Acad. Sci.* 893:13-18, 1999;
13. Yun-Zhong, F., Sheng, Y., Guoyao, W. Free radicals, antioxidants, and nutrition. *Nutrition.* 18:872-879, 2002.
14. Harman, D. Aging, a theory based on free radical andradiation chemistry. *J. Gerontology.* 11:298–300, 1956.
15. Kocić, G., Pavlović, D., Pavlović, R., Nikolić, G., Cvetković, T., Stojanović, I., Kocić, R. Sodium nitroprusside and preoxynitrite effect on hepatic DNases: An *in vitro* and *in vivo* study. *Comp. Hepatol.* 3(6):1-9, 2004.
16. Wyllie, AH. Glucocorticoid induced thymocyte apoptosis is associated with endogenous endonuclease activation. *Nature*. 284:555-556, 1981.
17. Fukuhara, M., Takabatak, E. *In vitro* inhibitory action of cadmium on microsomalmonooxygenases of rabbit lung, *Biochemical Pharmacology*. 31:3425–3429, 1982.
18. Mohammed-Brahim, B., Buchet, J.P., Bernard, A., Lauwerys, R. In vitro effects of lead, mercury and cadmium on the enzymic activity of red-blood cell pyrimidine 5'-nucleotidase. *Toxicology Letters.* 20(2):195-199, 1984.

BAT TECHNOLOGY IMPACT ON AIR QUALITY IN BOR

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ABSTRACT

Performance of BAT technology of copper production, when it comes to environmental protection, is best seen in air quality assessment in the area of impact. Assessment of air quality based on exceeding limit and tolerant values of pollutants is the only legally defined and binding assessment of the pollution level in the Republic of Serbia. In the long period of time air quality in Bor bwas classified as category III, ie, air was heavily polluted due to exceeded tolerance sulfur dioxide values. Research was focused on comparing sulfur dioxide concentrations at the City park measuring station in periods when production was conducted with the old technology compared to periods when copper was produced with the new BAT technology. Here presented are total annual sulfur dioxide emissions from the sulfuric acid plant and the smelter (old technology), and annual 2016 emissions from the sulfuric acid plant relative to the volume of processed concentrates. Assessment of air quality in Bor is given for the 2010-2016 period based on monitored average annual sulfur dioxide concentrations at the City Park station.

Key words: sulfur dioxide, BAT, tolerance values.

INTRODUCTION

In order to reduce emission of pollutants in the environment, primarily emissions in air and water, as well as to reduce production cost, reconstruction of the smelter was undertaken, which had been in operation since 1961 as the most modern at the time. In the period of the greatest prosperity of RTB Bor, in the eighties, output used to reach over 100 thousand tons of copper annually, and substantial SO_2 quantities and suspended particles containing heavy metals were emitted in the air. New flash-smelting technology was launched aiming at providing higher copper recovery, with designed furnace capacity of 80 thousand tons of cathode copper per year [1]. Technology was selected in line with best available technologies for this type of production. Capacity of the sulfuric acid plant was increased from 100 to 400 thousand tonnes per year [2]. Air pollution in Bor, which sometimes used to be a hundred times higher than limit values, is now reduced to permissible limits. Many studies have shown dependence of SO_2 concentrations in the ambient air on meteorological parameters, particularly the wind speed and direction, air temperature, humidity and atmosphere pressure. SO_2 as an air pollution indicator is a gas of strong smell and its toxicity increases with humidity, adversely affecting health of people, animals and plants [6-8].

MATERIALS AND METODS

One of the main criteria for assessing process performance in copper metallurgy is a possibility of sulfur recovery, and sulfur dioxide binding. This has a direct impact on air quality in zones of influence. Autogenous copper concentrate smelting processes allow for sulfur binding of more than 95% from the smelting feed. As the best available copper production technology, Outokumpu (FSF) process has been installed which is the autogenous smelting process of sulphide concentrates in a floating state. After smelting at the flash furnace, the converting process continues in Pears-Smith converters, which is discontinuous and autogenous based on oxidation reactions of metal sulphides present in the matte. At the sulfuric acid plant, from waste smelter gases which are tretaed in wet and dry electric filters, sulfuric acid is produced by a double conversion method and two-stage SO_2 gas absorption [2].

Air quality in Bor is measured in accordance with the Regulation on the conditions and requirements for air quality monitoring ("Off. Gazette of RS" no., 11/2010, 75/10 and 63/13) [3]. Air quality is monitored continuously at automatic measuring stations which measure the current (by minute) and average (hourly and daily) sulfur dioxide values. Data on SO_2 concentrations in the ambient air in real time can be monitored on the site www.sepa.gov.rs of the Environmental Protection Agency - monitoring arranged by the national network. At the measuring location of the City park, the following equipment was installed: DKK-TOA Corp. GFS, model 312E Ambient SO_2 Analyzer for automatic SO_2 monitoring in the ambient air. To control the sulfur dioxide content, classic acidimetric method of ISO 4219.4220 /, 1997 is used. At the automatic stations, sulfur dioxide is measured using a UV method of EN 14212. Air quality, within this monitoring activity is controlled by an authorized, independent organization of the "Institute of Mining and Metallurgy" Bor.

Air quality is assessed by measuring pollutants concentration in the air, with evaluation criteria in accordance with the Regulation on the conditions and requirements for air quality monitoring.

Table 1. Criteria for air quality assessment based on daily average concentration of pollutants

Pollutant / air quality	Excellent	Good	Acceptable	Polluted	Very polluted
	1	2	3	4	5
SO_2	0-50	50.1-75	75.1-125	125.1-187.5	>187.5

Air quality is assessed on the basis of average annual concentration of pollutants obtained owing to air quality monitoring in the national as well as local monitoring networks. Environmental Protection Agency has conducted categorization and it reads:

The first category, clean or slightly polluted air, air with no exceeded limit values for any pollutant.

The second category, moderately polluted air, air with exceeded limit values for one or more pollutants.

The third category, heavily polluted air, air with exceeded tolerance values for one or more pollutants.

Figure 1 shows a map of data indicating the Bor location with automatic measuring air quality control stations (AMSKV). To analyze SO_2 concentrations, measuring station of the "City Park" was selected, located in the city center with administrative, commercial and office buildings, as well as several elementary schools, kindergartens, town market, college and hospital.

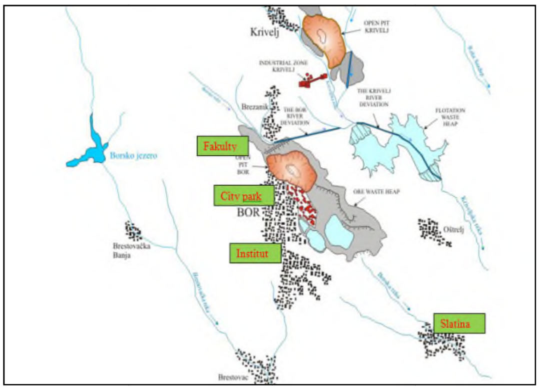

Figure 1. Layout of measuring points with AMSKV in the Bor area

Picture 2. Automatic measuring station „City park“

RESULTS AND DISCUSSION

SO_2 concentration data were analyzed at the "City Park" measuring station, located in the city center at about 850 meters southwest of the smelter stack, in the direction of the dominant east wind, which is one of the highest frequency winds during the year. There are administrative, commercial and office buildings, several elementary schools, kindergartens, town market, college and hospital. The old smelter and sulfuric acid plant ceased operation in early December 2015.

Pictures 3 and 4 show a view of the smelter stacks were taken during the operation of the old smelter (3) and the new BAT technology (4).

Picture 3. Bor with old technology in operation

Picture 4. with new technology in operation

Figure 5 shows annual average SO_2 concentrations measured at the measuring station of "City park", compared to annual limit values in the 1976-2016 period. SO_2 concentrations in the period when copper was produced with the old technology were ten times higher than in 2016 when production was conducted with the new BAT technology [5].

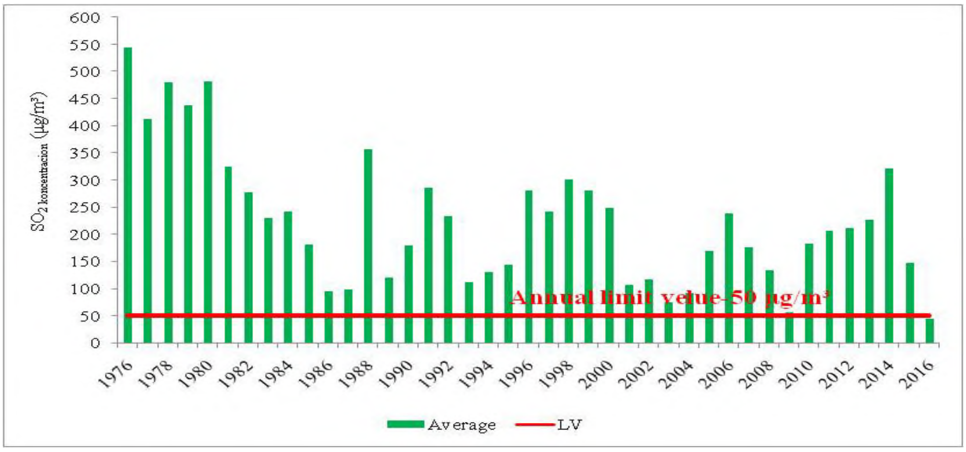

Figure 5. Average annual SO_2 concentrations (µg / m³) measured at the measuring station of "City park" in the 1976-2016 period

Figure 6 shows average monthly SO_2 concentrations at the measuring station of "City park" in 2016. Average annual SO_2 concentrations were within the limits (GV 50µg/m³)

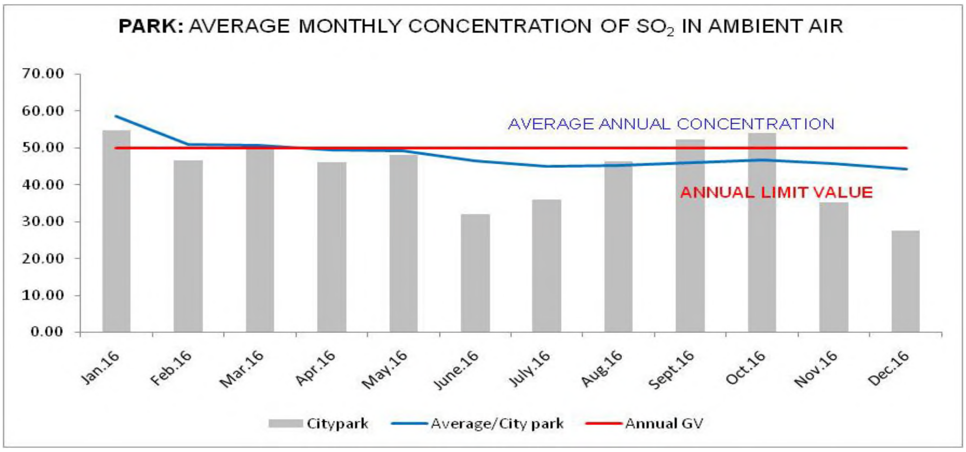

Figure 6. Average monthly SO_2 concentration (µg/m³) in the ambient air of the City Park

Figure 7 shows total annual SO_2 emissions in relation to the volume of treated concentrates in the 2008-2016 period

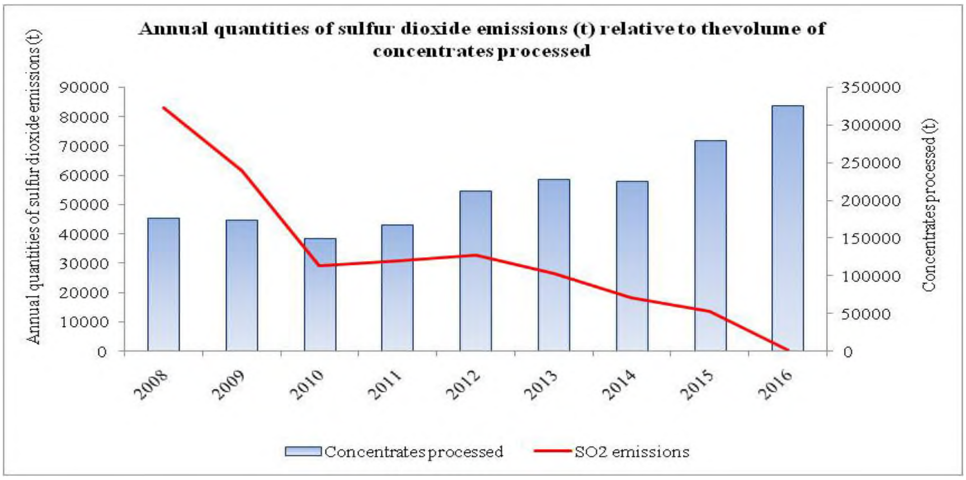

Figure 7. Annual quantities of sulfur dioxide emissions (t) relative to thevolume of concentrates processed in the 2008-2016 period

Figure 8 shows a total annual quantity of sulfur dioxide emissions (tons) from the smelter and sulfuric acid plant in the 2008-2016 period. The share of the SO_2 quantity emitted in 2016 compared to annual emissions in 2008 to 2015 was negligible.

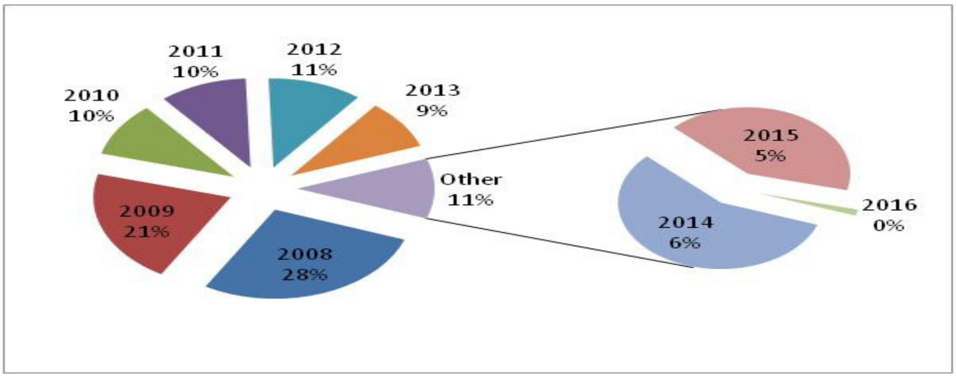

Figure 8. Total annual sulfur dioxide emissions from the smelter and sulfuric acid plant during the 2008-2016 period

Comparing average annual SO_2 concentrations in the period when copper was produced with old technology 1976-2015, in relation to 2016, when concentrates were processed and sulfuric acid produced with the new technology, when it comes to the measuring point of "City park", it can be concluded that in the period of the new technology, average annual SO_2 concentrations were ten times lower and are now within legal limits.

Comparing the total SO_2 quantity emitted throughout the year relative to the volume of processed concentrates, in the period when production was carried out with the old technology 2008-2015 in relation to 2016 when the concentrates wer processed and sulfuric acid produced with the new technology, it can be concluded that in the new technology period, significantly greater volume of concentrate was processed and considerably larger quanity of sulfuric acid produced, and at the same time total volume of emitted SO_2 was substantially reduced.

According to the data obtained from the Environmental Protection Agency [5] air quality in Bor in the 2010-2015 period, based on average measured annual sulfur dioxide concentrations at the measuring point of City Park, was category III (very polluted air).

In 2016 average annual sulfur dioxide concentrations at the measuring location of City park was below GVI and amounted to 43.6 µg/m thus belonging to air quality Category I.

CONCLUSION

The impact of the new BAT technology on air quality in Bor is very significant, as can be seen in the accompanying diagram. The performance of the new introduced technology is presented by the air quality assessment with respect to the average annual SO2 emitted concentrations and the total SO2 volume emitted per year from the smelter plant, relative to the quantity of processed concentrate in the period when production was conducted with the old technology, in the 2008 - 2015 period compared to 2016. It can be concluded that in the period of the new technology, significantly larger volume of concentrates were processed, and at the same time SO2 emissions were substantially reduced, indicating positive effects of the new smelter and sulfuric acid plant.

Air quality in Bor was for a long period of time categorized as category III, ie, air was heavily polluted due to exceeded tolerance sulfur dioxide values.

In 2016, average annual sulfur dioxide concentrations at the measuring location of City park was below GVI and amounted to 43.6 µg/m thereby air quality was classified as category I, which means clean or slightly polluted air, with limit values not exceeding for any pollutant.

REFERENCES

1. Studija o proceni uticaja na životnu sredinu Projekta "Rekonstrukcija topionice bakra i izgradnja fabrike za proizvodnju sumporne kiseline", Maj 2011.
2. IC TMF, Glavni tehnološki projekat dogradnje fabrike sumporne kiseline„ *Univerzitet u Beogradu, Beograd, 2014*
3. Uredba o uslovima za monitoring i zahtevima kvaliteta vazduha („Službeni glasnik RS", br.11/2010)
4. Institut za rudarstvo i metalurgiju Bor, Izveštaji o ispitivanju kvaliteta vazduha u Boru. Luvsan, M.E., Shie R.H., Purevdorj, T., Badarch L., Baldorj B., Chan C.C., 2012. The influence of emission sources and meteorological conditions on SO2 pollution in Mongolia. *Atmospheric Environment 61, 542-549*
5. Ministarstvo poljoprivrede i zaštite životne sredine, SEPA,Godišnji izveštaj o stanju kvaliteta vazduha u Republici Srbiji 2015. godine,
6. Wang, M., Zhu, T., Zhang, J.P., Zhang, Q.H., Lin, W.W., Li, Y., Wang, Z.F., 2011. Using a mobile laboratory to characterize the distribution and transport of sulfur dioxide in and around Beijing. *Athmospheric Chemistry and Physics 11, 11631-11645*
7. Mao, Q., Gautney, L.L., et al., 2006. Numerical experiments on MM5–CMAQ sensitivity to various PBL schemes. *Atmospheric Environment 40 (17), 3092–3110*
8. Speidel, M., Nau, R., et al., 2007. Sulfur dioxide measurements in the lower, middle and upper troposphere: deployment of an aircraft-based chemical ionization mass spectrometer with permanent in-flight calibration. *Atmospheric Environment 41 (11), 2427–2437*

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EFFECTS OF OXIDIZED NON-METALLIC FILLERS OBTAINED FROM WASTE PRINTED CIRCUIT BOARDS ON MECHANICAL PROPERTIES OF POLYESTER COMPOSITES

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ABSTRACT

Four different oxidized non-metallic fraction (NMF(1-4)) obtained from waste printed circuit boards (PCBs) were prepared by acid/base treatment. Such obtained material was used as a reinforcing filler for unsaturated polyester resin (UPR) synthesized from waste poly(ethylene terephthalate) (PET). The effect of oxidation process was investigated through comparison of mechanical properties of pure UPR, composite filled with untreated NMF and oxidized NMF particles. According to obtained results, significant improvement of tensile and micro hardness of UPR/NMF(1-3) composites are achieved, while addition of NMF4 slightly reduce the mentioned mechanical properties in respect to both, pure UPR and UPR/NMF composite. In this manner, the synergy of two different waste material (PET and NMF) is accomplished which justifies the physical recycling of NMF.

Key words: unsaturated polyester resin, non-metallic fraction, composites, mechanical properties, recycling.

INTRODUCTION

Unsaturated polyester resins (UPR) are one of the most used thermosetting polymers which have low cost, good stability and ability to undergo various post-polymerisation reactions [1]. These properties coupled with easy processing lead to the extensive usage of UPR as adhesives, tools, packaging and matrix materials for reinforced composites [2].

The high cross-linking degree of UPR makes it inherently brittle, causes relatively poor mechanical properties, which limits their application in advanced composites. The dynamic-mechanical, thermal and flame resistance properties of UPR can be improved by reinforcing with various types of organic/inorganic fillers such as glass fibers, inorganic minerals, natural and synthetic polymers and others [3–5].

One of the material which can be used in such purpose is non-metallic fraction (NMF) from printed circuit boards (PCBs). The hazardous nature of NMF makes recycling of this waste necessarily especially due to Brominated Flame Retardants (BFRs) content which could cause severe environmental issues [6]. Physical recycling processes for NMF treatment have many advantages comparing to chemical processes, as follows: relative simplicity, environmentally safe, with low investment costs in energy and equipment, and with diverse potential application of products obtained from recycled NMF. Potential applications for physically recycled NMF include usage as a filler in thermosetting and thermoplastic resins for improvement of thermo-mechanical properties and flame resistance due to BFRs content [7].

The main disadvantage of incorporation of pristine filler particles in resin matrix is poor physical-chemical filer/resin bondage which causes lower dynamic-mechanical properties of composites. Surface modification of the filler particles with physically (by physisorption) or chemically (through covalent bonding) routes have been employed to overcome this problem.

In this work, mechanical properties of composites based on UPR and acid/base treated NMF particles is presented.

EXPERIMENTAL PART

Synthesis of UPR - UPR was synthesized from waste poly(ethylene terephthalate) (PET) by glycolysis and afterwards polycondensation between obtained glycolytic product (polyol) and maleic anhydride was performed. The thoroughly described procedure for UPR synthesis from waste PET can be find elsewhere [5,8].

Acid/base treatment of NMF particles - The chosen NMF fraction for experiments shown in this paper contains particles with diameter size under 36 μm. The oxidized NMF were prepared analogously to previous published method [9]: ***NMF1***: $KMnO_4$ (1 g) was dissolved in 100 cm^3 of 0.5 mol dm^{-3} H_2SO_4. NMF (2 g) were dispersed (Bandelin electronic, Berlin, Germany, power 120 W, frequency 35 kHz) in 100 cm^3 of 0.5 mol dm^{-3} H_2SO_4 for one hour and after heating to 150 °C, the previously prepared $KMnO_4$ solution was added slowly. The NMF/$KMnO_4$ mixture solution was refluxed for 5 h at 150 °C. Finally, HCl (10 cm^3 of 35 %) was added to cooled reaction mixture for removal of MnO_2 byproduct. *NMF2*: NMF (2 g) was added to 88 cm^3 of acids mixture solution (H_2SO_4 (98 %)/HNO_3 (65 %), v/v 2:1) and then dispersed at 40 °C for 3 h. *NMF3*: NMF (2 g) was added in 80 cm^3 of 10 % NaOH and dispersed at 80 °C for 1 h. *NMF4*: NMF (2 g) was dispersed in 100 cm^3 of 65 % HNO_3 for 1 h, followed by refluxing at 140 °C for 1 h. All product was purified by washing with distilled water and filtration. After multiple filtration, oxidized NMF particles were dried in a vacuum oven at 80 °C for 2 h.

Preparation of composites based on UPR and oxidized NMF particles - Firstly, NMF(1-4) was dispersed in styrene (12 wt.% in relation to UPR) using ultrasonic for 10 min. In order to prevent styrene evaporation, ice was periodically added into ultrasonic bath. Then, UPR (72 wt.% in styrene) was added in three equal portions (3 g in total) and homogenized with NMF in styrene, using modified laboratory homogenizer for 10 min. Before adding of new UPR portion, obtained slurry was treated in ultrasonic bath for 10 minutes. Finally, when the entire amount of UPR was added and homogenized with NMF(1-4), accelerator (cobalt octoate, 0.5 wt.% with respect to UPR) and catalyst (MEKP, 1.5 wt.% with respect to UPR) were added followed by vigorous stirring (800 rpm) for 1 min. The obtained mixture was cured in a poly(tetrafluoroethylene) (PTFE) mould at room temperature and atmospheric conditions for 4 h and post-cured at 50 °C for an additional 2 h.

Experimental techniques - The structural analysis of oxidized NMF fillers were performed using Fourier transform infrared (FTIR) spectroscopy (Bomem MB-102), within a range of 400-4000 cm^{-1}, at a resolution of 4 cm^{-1}. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of UPR were recorded in deuterated chloroform ($CDCl_3$), using a Varian-Gemini 2000 spectrometer at 200 MHz for the ^{1}H NMR and 50 MHz for the ^{13}C NMR spectra. Uniaxial tensile measurements of standard cured samples (ASTM D882-12) were performed using an AG–X plus Universal testing machine, Shimadzu Corporation. All tests were performed at room temperature adjusted at crosshead speed of 0.5 mm/min. All uniaxial tensile measurements were performed on three replicates for each sample. The hardness of the composite systems was characterized using micro Vickers hardness (HV) tester Leitz, Kleinharteprufer DURIMETI with a load of 4.9 N (HV 0.5/25 – where the value 0.5 is the load in kgf, and 25 is a loading time in second), using an original quadrangular pyramid diamond indenter with an angle of 136°.

RESULTS AND DISCUSSION

FTIR - The FTIR spectra of treated NMF(1-4) are shown in Fig. 1. The broad peak for all NMF particles at > 3000 cm^{-1} corresponds to hydroxyl (OH) groups stretching vibrations. Overlapped symmetric and asymmetric vibrations of methyl (CH_3) and methylene (CH_2) groups are observed about 2927 cm^{-1} and 2851 cm^{-1}. The of peaks at 1463 cm^{-1} and 1388 cm^{-1} correspond to stretching and bending vibrations of CH_3 and CH_2 groups, respectively. The characteristic C=C stretching vibrations of benzene ring present in bisphenol A are observed at 1620 cm^{-1} and 1508 cm^{-1}. The peak at 1243 cm^{-1}, which is disappeared in NMF4, originates from C-O vibrations, while peak at 1031 cm^{-1} originates from C-O stretching which represents molecular backbone of the modified epoxy resin contains anisole-like moiety [10]. The peak at 1347 cm^{-1} indicates introduction the nitro groups onto NMF particles surface (NMF2 and NMF4) while peak at 1384 cm^{-1} correspond to vibration of sulfonic (OSO_3H) group and OH from COOH groups (NMF1 and NMF2). The peak at 668 cm^{-1} originates from C-Br stretching vibrations in tetrabromobisphenol A moiety (TBBP A), which is reactive flame retardant incorporated in epoxy resin.

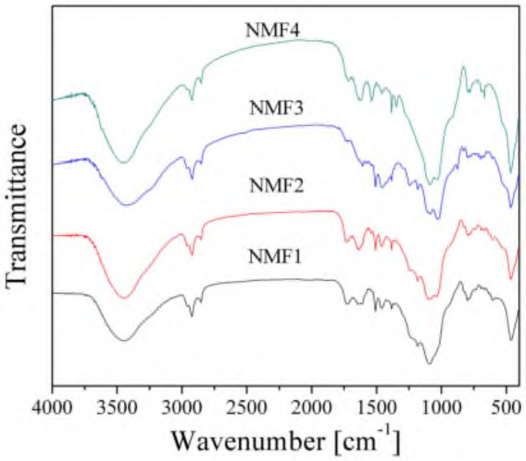

Figure 1. FTIR spectra of NMF(1-4)

NMR - ^{1}H and ^{13}C NMR analysis was applied to confirm structure of obtained UPR, and corresponding spectra indicate that UPR contains mostly more reactive fumaric moiety necessary for achieving high cross-linking reactivity during molding/sample formation. Results of ^{1}H and ^{13}C NMR analysis (Figure S1) of UPR are as follow:

^{1}H NMR ($CDCl_3$): 1.24-1.52 (*m*, 6H, 2×C$\underline{H}_3$), 4.11-4.59 (*m*, 6H, 2×C$\underline{H}_2$C$\underline{H}$–), 4.26-4.71 (*m*, 4H, –O–C$\underline{H}_2$C$\underline{H}_2$–O–), 5.29-5.43 and 6.86 (*m*, 2H, fumaric moiety), 8.09 (*s*, 4H,HPh-terephthaloyl moiety);

^{13}C NMR ($CDCl_3$): 16.31 and 19.22 (2×$\underline{C}H_3$), 62.74, 66.55-69.23, 76.37, 77.01 and 77.64 (CH_2 carbons in PG moiety), 129.66 (4×CPh), 133.58 (2×Ph($\underline{C}$)–COO), 134.01 (O=C–H$\underline{C}$=$\underline{C}$H–C=O), 164.1 and 164.42 (O=$\underline{C}$–HC=CH–$\underline{C}$=O), 165.01 and 165.15 (2×Ph$\underline{C}$OO).

^{1}H and ^{13}C NMR spectra of the synthesized UPR show that the dominant products of glycolysis were glycol esters of terephthalic acid: *bis*(2-hydroxylpropyl) terephthalate,(2-hydroxyethyl)(2-hydroxypropyl) terephthalate and glycols. Results of NMR analysis confirm successful synthesis of UPR.

Mechanical testing of UPR/NMF(1-4) composites - Mechanical testing was performed in order to investigate influence of geometry and properties of treated NMF particles on the mechanical characteristics of the obtained composites. The values of tensile stress at break (σ_t), elongation at break (ε_t), tensile modulus (E_t) as well as micro hardness values are shown in Table 1, respectively. All results are presented in respect to pure UPR and composite with untreated NMF for better understanding the reinforcing effect of oxidized NMF particles. Appropriate relation of tensile strength and micro Vickers hardness *versus* type of composites is given in Fig. 2.

Table 1. Tensile stress at break (σ_t), elongation at break (ε_t), tensile modulus (E_t) and micro hardness values of UPR, UPR/NMF and UPR/NMF(1-4) composites

Sample	σ_t [MPa]	ε_t [%]	E_t [GPa]	HV [kgf/mm^2]
UPR	31.23±0.73	3.06±0.13	1.15±0.07	25.21±0.28
UPR/NMF	29.53±1.46	3.32±0.14	1.30±0.06	30.54±0.58
UPR/NMF1	31.28±0.97	3.54±0.14	0.88±0.05	33.69±1.67
UPR/NMF2	33.36±0.61	3.80±0.12	0.90±0.05	35.67±0.70
UPR/NMF3	36.84±0.38	3.55±0.13	1.03±0.08	35.11±2.64
UPR/NMF4	28.49±0.68	3.04±0.12	1.03±0.06	33.05±0.70

It is observed from Table 1 that addition of NMF(1-3) gradually increased, while incorporation of NMF4 decreased the tensile strength. The effect of NMF treatment is even more pronounced if those results compare with composite filled with untreated NMF particles. The improvement of σ_t was in range from 6.8 to 18.0 % and from 5.9 to 24.7 % compared to pure UPR and UPR/NMF composite, respectively. According to data for ε_t, more flexible materials were obtained by incorporation of treated NMF, which was reflected in decreasing of tensile modulus.

Micro Vickers hardness of UPR/NMF(1-4) showed similar behavior as the tensile strength, depending on the type of added NMF particles: the highest value had composites with NMF2 and NMF3, while composite with NMF4 showed the lowest value. Still, shown values were higher compared with those for pure UPR and UPR/NMF composite. Increase of HV values was in range from 31.1 % to 41.5 % and from 8.2 % to 16.8 % in relation to pure UPR and UPR/NMF composite, respectively. Those observations indicated improved interfacial resin matrix/filler particles bonding which led to significant reinforcing effect reflected through higher σ_t and HV values. Acid/base treatment of NMF led to improving the compatibility between UPR matrix and fillers causing better interfacial adhesion and thus, better mechanical properties.

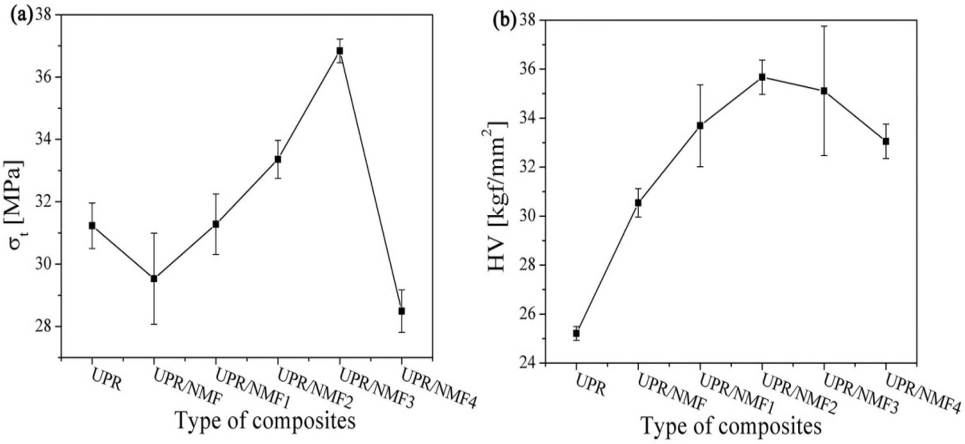

Figure 2. (a) Tensile strength and (b) micro Vickers hardness as a function of type of composites

CONCLUSION

The main purpose of this work is to investigate reinforcing effect of modified NMF particles when they are incorporated in UPR matrix synthesized from waste PET. According to obtained results, significant improvement of tensile and micro hardness of UPR/NMF(1-3) composites are achieved, while addition of NMF4 slightly reduce the mentioned mechanical properties in respect to both, pure UPR and UPR/NMF composite. In this manner, the synergy of two different waste material (PET and NMF) is accomplished which justifies the physical recycling of NMF.

Acknowledgements

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REFERENCES

1. S. Chaeichian, S. Pourmahdian, F.T Afshar (2008) Synthesis of unsaturated polyester resins from PET wastes: effect of a novel Co-catalytic system on glycolysis and polyesterification reactions, Des Monomers Polym 11, 187–199
2. R.P. Singh, M. Zhang, D. Chan (2002) Toughening of a brittle thermosetting polymer: Effects of reinforcement particle size and volume fraction, J Mater Sci, 37, 781–788
3. S. Hong, S. Su (1996) The use of recycled printed circuit boards as reinforcing fillers in the polyester composite, J Environ Sci Heal Part A, 1345–1359.
4. L. Devi, S. Bhagawan, S. Thomas (2010) Dynamic mechanical analysis of pineapple leaf/glass hybrid fiber reinforced polyester composites, Polym Compos, 31, 956–965
5. J.D. Rusmirović, T. Radoman, E.S. Džunuzović, J.V. Džunuzović, J. Markovski, P. Spasojević, A.D. Marinković (2017) Effect of the modified silica nanofiller on the mechanical properties of unsaturated polyester resins based on recycled polyethylene terephthalate, Polym Compos, 38, 538–554
6. D. Wang, Z. Cai, G. Jiang (2005) A. Leung, M.H. Wong, K.W. Wai. Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility, Chemosphere, 60,810–816
7. P. Kanchanapiya, W. Pinyo, S. Jareemit, S. Kwonpongsagoon (2015) Recycling of non-metallic powder from printed circuit board waste as a filler material in a fiber reinforced polymer, Environ Prot Eng, 41,151–166
8. M. Lu, S. Kim (2001) Unsaturated polyester resins based on recycled PET: Preparation and curing behavior, J Appl Polym Sci, 80,1052–1057
9. V.R. Djokić, A.D. Marinković, M. Mitrić, P.S. Uskoković, R.D. Petrović, V.R. Radmilović, Đ.T. Janaćković (2012) Preparation of TiO_2/carbon nanotubes photocatalysts: The influence of the method of oxidation of the carbon nanotubes on the photocatalytic activity of the nanocomposites, Ceram Int, 38,6123–6129
10. Z. Wu, S. Li, M. Liu, Z. Wang, X. Liu (2015) Liquid oxygen compatible epoxy resin: modification and characterization. RSC Adv, 5,11325–11333

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ELECTROCHEMICAL BEHAVIOR OF COPPER IN PRESENCE OF CHESTNUT MACERATE

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ABSTRACT

Electrochemical behavior of copper has been investigated by measuring the open circuit potential and using anodic sweep voltammetry method in pure 0.5 mol/dm^3 NaCl, as well as in 0.5 M mol/dm^3 NaCl with the addition of chestnut macerate in different concentrations. Anodic polarisation curves show that three current peaks, which correspond to formation of chlorides and oxides of copper, appear on voltammograms. Current density of those peaks descreases with the increasing chestnut macerate concentration in electrolyte, pointing at inhibition properties of the substances present in water extract of powder obtained by grounding chestnut fruits.

Key words: copper, electrochemical behavior, green inhibitors, chestnut.

INTRODUCTION

Corrosion of metals causes numerous negative technical and economic consequences. On the other hand corrosion products have negative ecological effects. Because of that, attempts are made to slow down those processes, use of corossion inhibitors being one of methods. The most effective among inhibitors for copper and its alloys are compounds from the azole group [1-4]. Those compounds, as well as the other organic substances which have inhibitive properties, are usually toxic with their own negative ecologic effects. This is the reason because in recent years extensive investigations are targeted on discovering corrosion inhibitors acceptable from the ecologic point of view.

Extract from some parts of plants such as root, stalk, fruit, seed, leaf, tree bark or flower, can be a possible solution. Those parts of herbs often contain organic substances which can be extracted in solution by an adequate method. The obtained solutions can be used to slow down corrosion of some metals.

Copper and its alloys are in greate extent resistant to corrosion in meny different environments. The exception are solutions containing chloride ions, where copper is subjected to corrosion, so a great number of authors investigated copper behavior in chloride solutions [4-6]. The possibility to slow down copper corrosion using some organic inhibitors, nowdays with special attention on so-called green inhibitors, is a subject of meny scientific papers [7-11]. This paper presents the results of investigation of influence of macerate obtained from chestnut fruit on electrochemical behavior of copper in a chloride solution.

EXPERIMENTAL

The electrochemical behavior of copper was investigated in 0.5 mol/dm^{3}NaCl with the addition of chestnut macerate in different concentrations, as well as in pure 0.5 mol/dm^3 NaCl by measuring open circuit potential in reference to saturated calomel electrode (SCE) during 60 s. Anodic polarisation curves are recorded in a potential range from -0.4 V vs SCE to +1V vs SCE using the scan rate of 20 mV/s.

The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control and data acquisition. In a standard three-electrode electrochemical cell, the working electrode was Cu, whose potential was controlled against saturated calomel reference electrode (SCE). Platinum foil served as a counter electrode. The computerized control (National Instruments card, NI-6251) and data acquisition software (LabVIEW 8.2 platform), fully developed by Technical Faculty in Bor [12], was used to run the electrochemical experiments.

Chemicals used in this work for preparation of working solutions are NaCl of p.a. purity (product by „Zorka Pharma" Šabac, Serbia), grinded and prepared chestnut fruit (product by "Adonis", Sokobanja, Serbia) and distilled water. Macerate is obtained by the following procedure: 25 g of ground chestnut is added in 500 mL distilled water heated to 60 ºC. Extraction is performed by mixing on magnetic stirrer during 3 hours keeping the temperature on 60 ºC all the time. Obtained solution is filtered on vacuum filter and kept in the fridge. Working solutions are prepared with the addition of 10 to 100 mL of macerate in 1 L of solution taking into account that the concentration of sodium chloride must remain constant (0.5 mol/dm^3).

RESULTS AND DISCUSSION

Open circuit potentials measurement in 0.5 mol/dm^3 NaCl, with and without the addition of chestnut macerate, is resulted with the curves presented in Figure 1. It can be seen from the figure that the open circuit potential for pure copper is E = -0.313 V vs. SCE. With the addition of the chestnut macerate the open circuit potential of copper becomes more positive reaching from -0.198 to -0.187 V vs. SCE. It is obvious that already minimal added quantities of chestnut macerate moves copper potential to significantly higher values.

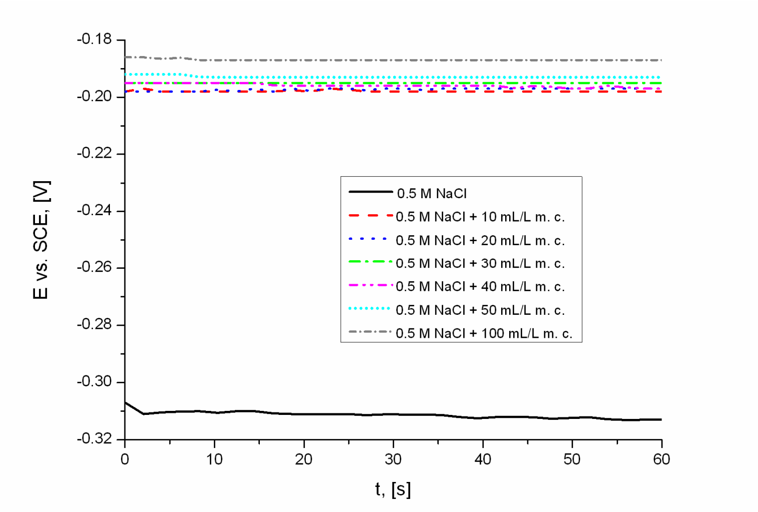

Figure 1. Open circuit potential of copper in 0.5 mol/dm^3 NaCl, with and without the addition of chestnut macerate

Anodic polarisation curves recorded for pure copper with the scan rate of 20 mV/s in 0.5 mol/dm^3 NaCl, with and without the addition of chestnut macerate, are presented in Figure 2. On the polarisation curve recorded for pure copper three anodic current peaks marked as A_1, A_2 i A_3 appear. Comparing with the published results obtained in the same conditions, it can be assumed that current peaks A_1 and A_2 correspond to formation of copper chlorides by the following mechanism [6, 13-15]:

$$Cu + Cl- = CuClads + e \qquad (1)$$
$$CuCl_{ads} + Cl^- = CuCl_2^- \qquad (2)$$
$$Cu + CuCl_2^- = 2CuCl + e^- \qquad (3)$$

During the anodic polarisation always exists the equilibrium between species CuCl i $CuCl_2^-$.

After the Pourbaix diagram for copper in chloride solutions it can be assumed that current peak A_3 should be assigned to formation of cuprous oxide Cu_2O by the following mechanism [16]:

$$CuCl + 2OH^- = Cu_2O + 2Cl^- + H_2O \qquad (4)$$

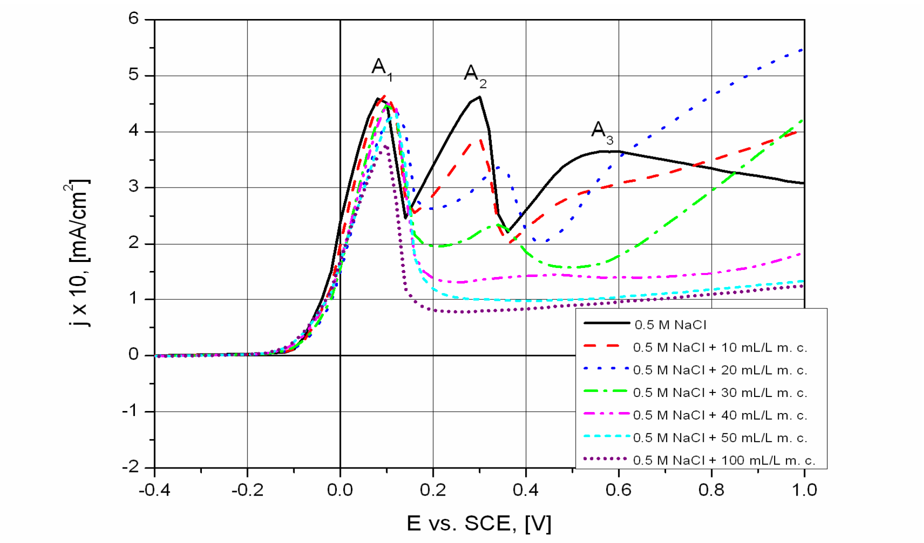

Figure 2. Anodic polarisation curves for pure copper in 0.5 mol/dm^3 NaCl, with and without the addition of chestnut macerate; scan rate 20 mV/s

Peak current densities on polarisation curves recorded in the presence of chestnut macerate are lower than those obtained in pure sodium chloride solution. Increasing chestnut macerate concentration leads to shifting of the current peaks potential to more positive values, while when that concentration overcomes 30 mL/L, current peaks A_2 and A_3 do not appear. These effects point at the inhibition properties of substances present in chestnut extract in water on copper corrosion in chloride solutions.

CONCLUSION

The experiments presented in the paper resulted with the following conclusions:

1. The addition of the chestnut macerate in 0.5 mol/dm^3 NaCl shifts the open circuit potential of copper to more positive values for about 120 mV.
2. On the potentiodynamic polarisation curve recorded for pure copper in 0.5 mol/dm^3 NaCl appear three anodic current peaks, which are ascribed to formation of two chlorides of copper and cuprous oxide as an oxidative species.
3. On polarisation curves recorded in the presence of chestnut macerate current peaks appear at more positive potentials, but with lower current densities then those recorded in pure chloride solution of the same concentration pointing at the inhibition properties of substances present in the chestnut extract.

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REFERENCES

1. Zhang D., Gao L., Zhou G., Inhibition of copper corrosion by bis-(1-benzotriazolymethylene)-(2,5-thiadiazoly)-disulfide in chloride media, Applied Surface Science, 225, p. 287-293, 2004.
2. Abdullah A. M., Al-Kharafi F. M., Ateya B. G., Intergranular corrosion of copper in the presence of benzotriazole, Scripta Materialia, 54, p. 1673-1677, 2006.
3. Hao Y. Z., Yang M. Z., Yu C., Cai S. M., Zhou G. D., The effects of chloride ions and benzotriazole on photoresponses of copper electrodes, Thin Solid Films, 347, p. 289-294,1999.
4. Tromans D., Sun R, Anodic polarization behavior of copper in aqueous chloride/benzotriazole solutions, Journal of the Electrochemical Society, 138, 11, p. 3235-3244 , 1991.
5. Kear G., Barker B. D., Walsh F. F., Electrochemical corrosion of unalloyed copper in chloride media a critical rewiew, Corrosion Science, 46, p. 109-135, 2004.
6. Otmačić H., Stupnišek-Lisac E, Copper corrosion in near neutral media, Electrochemica Acta, 48, p. 985-991, 2003.
7. Bozorgt M., Farahani T.S., Neshati J., Myrtus Communis as green inhibitor of Copper corrosion in Sulfuric Acid, Materials Engineering Department, Faculty of Engineering, Tarbiat Modares University, Tehran, Iran, 2014.
8. El-Haddad Mahmoud N., Chitosan as a Green Inhibitor for Copper Corrosion in Acidic Medium, Chemistry Faculty of Science, Mansoura Univerzity, Mansoura, Egypt, 2012.
9. Fouda A. S., El-Haddad M. N., Abdallah Y. M., Septazole: Antibacterial drug as a Green corrosion inhibitor for Copper in hydrochloric Acid Solution, Department of chemistry, Faculty of Science, Mansoura university, Mansoura, Egypt, 2013.
10. Palou R. M., Homelt O. O., Likhanova N. V., Environmentally Friendly Corrosion Inhibitors, Developments in Corrosion Protection, Edited by M. Aliofkhazraei, InTech, p. 431-463, 2014.
11. Sham A. M., Rahim A. A., Hamid S. A., Yahya S., Green Inhibitors for Copper Corrosion by Mangrove tannin, School of Chemical Sciences, University Sains Malaysia, Penang, Malaysia, 2013.
12. Stević Z., Rajčić-Vujasinović M., System for electrochemical investigations based on a PC and the labVIEW package, Chemical Industry, 61, p. 1-6, 2007.
13. Kosec T., Milosev I., Pihlar B., Benzotriazole as an Inhibitor of Brass Corrosion in Chloride Solution, Applied Surface Science, 253, p. 8863–8873, 2007.
14. Mamas S., Kıyak T., Kabasakaloglu M., Koc A., The Effect of Benzotriazole on Brass Corrosion, Materials Chemistry and Physics, 93, p. 41–47, 2005.
15. Grekulović V., Rajčić –Vujasinović M., Electrochemical Behavior of AgCu Alloy in Alkaline Medium in the Presence of Chloride Ions, Corrosion, 68, 2, p. 025003-1 - 025003-8, 2011.
16. Pourbaix M., Atlas d'equilibres Electrochimiques, Gauthier-Villars et Cie, Paris, 1963.

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EQUILIBRIUM STUDY OF Sr^{2+} AND Pb^{2+} IONS SORPTION USING BONE-APATITE OF VARIOUS VERTEBRATE SPECIES

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ABSTRACT

Hydroxyapatite (HAP) is a calcium-phosphate mineral with the capacity to bond a variety of metal cations. As a rich source of biogenic HAP, bones are the main reservoir for accumulation of heavy metals and radionuclides in the body of vertebrates. This feature of bone tissue can be beneficially utilized for selective immobilization of pollutants. In this study, the sorption capacities of pork, bovine, chicken and fish bones were preliminary tested in respect to Sr^{2+} and Pb^{2+} ions, due to significance of ^{90}Sr and ^{210}Pb isotopes as radioactive contaminants. Mathematical description of equilibrium sorption data showed different affinity of bio-HAP towards investigated ions at lower and at higher concentrations. Maximum sorption capacities were dependent on the bones origin, however, fish bones exhibited highest capacity for both Sr^{2+} and Pb^{2+} ions.

Key words: bones, apatite, Sr^{2+}, Pb^{2+}, separation.

INTRODUCTION

The bones of vertebrates represent a complex organic/inorganic composite of approximately 60-70% of biological calcium-phosphate in the form of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), and the organic matter, mainly protein collagen [1, 2]. In recent years, hydroxyapatite (HAP) has become one of the most investigated materials due to a variety of potential uses. Biocompatibility, bioactivity and osteoconductivity of such material are important characteristics in medical applications [3, 4], while the ability to retain a variety of cationic and anionic species finds use in waste treatment and environmental protection[5-7]. Therefore, bones collected as meat and fishery industry waste have prospective for recovery and valorisation of HAP mineral.

Expressed sorption potential of biological apatite with respect to the number of radionuclides has been reported [8-10]. In the presence of HAP phase, precipitation and ion-exchange reactions control radionuclide speciation by their conversion from soluble form to highly insoluble radionuclide-phosphate minerals. In this regard, isotopes of ^{90}Sr and ^{210}Pb are particularly interesting, due to their radiochemical properties. ^{90}Sr is the fission product which is among the most common contaminants of groundwater and soil, and also one of the most common isotopes in liquid effluents from nuclear plants. ^{210}Pb is a naturally occurring radionuclide of the ^{238}U series. Both isotopes have an important role in human radiation exposure because ^{90}Sr and ^{210}Pb deposit in the skeleton long enough and thus highly contributes to skeletal dose. Therefore their elimination from any part of environment (water, soil, air) is necessary to prevent human food chain contamination.

In this study, sorbents derived from bones of several vertebrate species were preliminarily compared in respect to their binding capability of Sr^{2+} and Pb^{2+} ions from aqueous solutions. The study of the interactions between bone HAP and the aqueous solution of the radionuclides is significant from the viewpoint of pollutants retention in living organisms, as well as in terms of radionuclide separation for *analytical purposes and* treatment of contaminated effluents.

MATERIALS AND METHODS

Row bones of various species, namely pork (PB), bovine (BB), chicken (CB) and fish (FB), were collected at a local market. Meat residues were separated and discarded, while the bones were chopped to small pieces and separately cooked in distilled water for an hour. This procedure was repeated four times, to remove soluble organics. Such samples were dried in the oven at 50°C, and then milled and sieved to the same size fraction (200 - 250 µm). In this way, four different powders were obtained and subsequently used as sorbents.

Sorption experiments were conducted in batch mode using stable isotopes of Sr^{2+} and Pb^{2+}. Solutions of different Sr^{2+} and Pb^{2+} concentrations in the range 10^{-5} - 10^{-2} mol/L were prepared by dissolving $Sr(NO_3)_2$ and $Pb(NO_3)_2$ salts of analytical purity in deionized water. The initial pH value of each prepared solution was adjusted to 5.0±0.2 by adding small amounts of 0.01 mol/L NaOH or HNO_3. The contact between sorbents (0.100 g) and metal solutions (20 mL) was made in 50 mL centrifuge tubes, which were placed on the overhead laboratory shaker, and agitated at 10 rpm for 24 h, to assure equilibrium conditions. All experiments were conducted at ambient temperature (20±1°C). After specified time interval, solid/liquid separation was accomplished by centrifugation and the clear supernatants were used for pH measurements and determination of the residual metal concentrations by Perkin Elmer 3100 Atomic Absorption Spectrophotometer (AAS). As an indicator of exchange stoichiometry between sorbed and released cations, the concentration of Ca^{2+} ions, released from the sorbent materials, were measured as well. The sorbed amounts of selected ions were calculated by subtracting the residual concentrations of the initial ones, and expressed in mmol per gram of sorbent.

RESULTS AND DISCUSSION

Experimental results on Pb^{2+} and Sr^{2+} removal from the solutions of increasing initial concentrations are presented in the form of sorption isotherms (Fig. 1A and Fig. 2A). The amounts of cations retained in solid phase have increased with the increase of equilibrium concentrations in the solution. Sr^{2+} isotherms were similar in shape, with a gradual increase of sorbed quantities, whereas isotherms of Pb^{2+} sorption were generally characterized by higher initial slopes and expressed plateaus.

Changes in solution pH are presented in respect to the quantity of sorbed metals (Fig. 1B and Fig. 2B). The increase in sorption was followed by decline in equilibrium pH. Commonly, the pH values were in near neutral pH range (6.5-7.5) after contact with sorbent materials, except for high Pb^{2+} uptakes for which pH declined to ~5, in all investigated systems.

The increase of aqueous Ca^{2+} concentrations was linearly correlated with increased sorption of both ions (Fig. 1C and Fig. 2C). This is an indication of the Sr^{2+} and Pb^{2+} incorporation in phosphate mineral by ion-exchange or dissolution/precipitation mechanism. Ca^{2+} substitution with Sr^{2+} ions was previously reported for both synthetic [11] and bone derived apatites [12]. Pb^{2+} removal can be driven by surface complexation and ion-exchange at lower initial concentrations [13], however, dissolution of HAP and precipitation of less soluble Pb-apatite (hydroxypyromorphite) can also be an operating mechanism, especially at higher concentrations of Pb^{2+} [14].

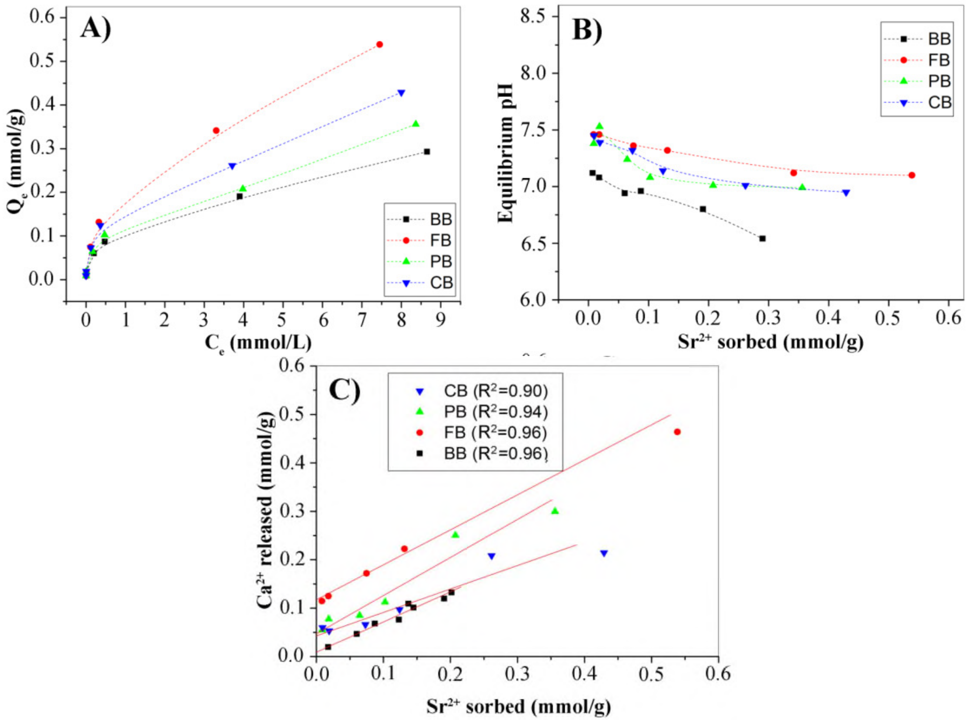

Figure 1. (A) Sorption isotherms of Sr^{2+} ions on different animal bones, (B) relationships between the amount of sorbed $Sr^{2+}$and equilibrium pH values, (C) linear fitting of Sr^{2+} sorbed and Ca^{2+} released amounts.

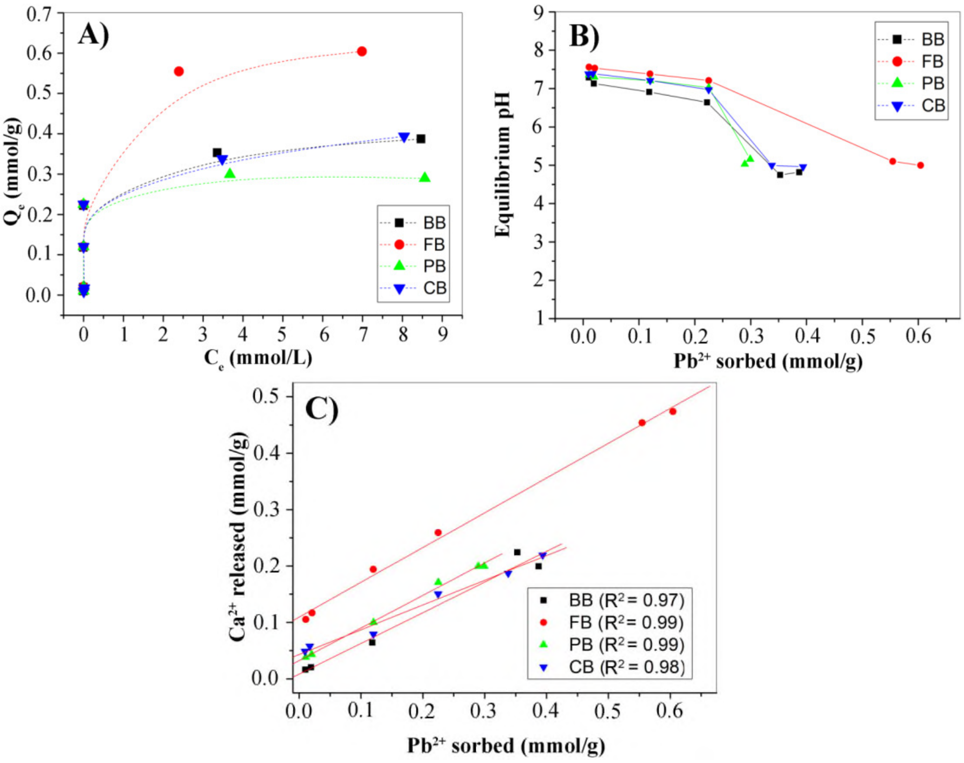

Figure 2. (A) Sorption isotherms of Pb^{2+} ions on different animal bones, (B) relationships between the amount of sorbed Pb^{2+} and equilibrium pH values, (C) linear fitting of Pb^{2+} sorbed and Ca^{2+} released amounts.

In order to describe experimental results mathematically, sorption data were analyzed in accordance with Langmuir (Eq. (1)) [15] and Freundlich (Eq. (2)) [16] linear equations, frequently used for modelling sorption processes at solid/liquid interface.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}} \tag{1}$$

$$\log Q_e = \log K + n \log C_e \tag{2}$$

In Eq. 1 and 2, Q_e (mmol/g) denotes the quantity of Sr^{2+} and Pb^{2+} ions sorbed per mass of bone sorbents at equilibrium; C_e (mmol/L) is the equilibrium concentration in solution, Q_m (mmol/g) is the maximum sorption capacity, K_L (L/mmol) is the Langmuir constant related to affinity, while K_f and n are Freundlich constants associated with sorption capacity and intensity.

The results (Table 1) have revealed several essential characteristics of the investigated systems. Experimental data for Sr^{2+} ions were better fitted by Freundlich model, whereas results for Pb^{2+} ions followed the Langmuir model, irrespective of the bone origin.

Significantly higher K_L values obtained for Pb^{2+} ions reflect higher affinity of all investigated sorbents towards this cation, especially in the regions of lower Q_e and C_e values. Maximum sorption capacities, Q_m, were in the range 0.305-0.555 mmol/g for Sr^{2+} ions and decreased in the order FB>CB>PB>BB. Different trend was obtained for Pb^{2+} ions FB>CB≈BB>PB, and the range was 0.291-0.602 mmol/g. Results imply that maximum sorption capacity significantly differed between bone samples, with FB showing highest maximum capacity compared to the bones of other investigated species.

Table 1. Parameters of Pb^{2+} and Sr^{2+} sorption by various bone sorbents calculated according to Langmuir and Freundlich isotherm models.

Sorbent	Langmuir model			Freundlich model		
	Q_m (mmol/g)	K_L (L/g)	R^2	n	K_f ($mmol^{1-n}$ dm^{3n} g−1))	R^2
	Sr^{2+}					
FB	0.555	1.253	0.950	0.554	0.198	0.981
PB	0.350	1.252	0.912	0.451	0.131	0.986
CB	0.422	1.572	0.931	0.442	0.170	0.991
BB	0.305	1.032	0.949	0.409	0.116	0.998
	Pb^{2+}					
FB	0.602	32.79	0.999	0.124	0.452	0.734
PB	0.291	284.9	0.999	0.129	0.159	0.197
CB	0.397	4.490	0.994	0.178	0.164	0.202
BB	0.384	25.55	0.998	0.044	0.343	0.992

CONCLUSION

The powdered bovine, pork, chicken and fish bones were compared as sorbents for aqueous Sr^{2+} and Pb^{2+} ions under equilibrium conditions. The shapes of the Pb^{2+} sorption isotherms fitted the Langmuir model, whereas Sr^{2+} sorption was better described using Freundlich equation. Bones generally exhibit higher affinity for Pb^{2+} ions in lower concentration range. Maximum sorption capacities depended on the origin of bone sorbent, nevertheless, the capacities of fish bones were highest considering both investigated ions, reaching 0.555 mmol/g and 0.602 mol/g, respectively for Sr^{2+} and Pb^{2+}. The results indicate that animal, and especially fish bones, collected as a waste, could be transformed into high capacity radionuclide sorbents.

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REFERENCES

1. Wopenka B.T., Pasteris J.D., 2005, A mineralogical perspective on the apatite in bone, Mater. Sci. Eng. C, 25, 131–143.
2. Boskey A.L., 2013, Bone composition: relationship to bone fragility and antiosteoporotic drug effects, BoneKEy Reports 2, Article number: 447.
3. Hydroxyapatite (HAp) for Biomedical Applications, 2015, Edited by Michael Mucalo, Woodhead Publishing Series in Biomaterials: Number 95, 450 p., Elsevier, Amsterdam.
4. Lin X., de Groot K.,Wang D., Hu Q., Wismeijer D., Liu Y., 2015, A review paper on biomimetic calcium phosphate coatings, Open Biomed Eng. J. 9, 56–64.
5. Kizilkaya B., Tekinay A.A., Dilgin Y., 2010, Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones. Desalination 264, 37–47.
6. Hodson M.E., Valsami-Jones E., Cotter-Howells J.D, 2000, Bonemeal additions as a remediation treatment for metal contaminated soil, Environ. Sci. Technol. 34, 3501–3507.
7. Martinez R.J., Beazley M.J., Sobecky P.A., 2014, Phosphate-mediated remediation of metals and radionuclides, Advances in Ecology, 2014, Article ID 786929, 14 pages.
8. Park Y., Shin W.S., Choi SJ.J., 2013, Removal of cobalt and strontium from groundwater by sorption onto fishbone. J. Radioanal. Nucl. Chem. 295, 789–799.
9. Fuller C.C., Bargar J.R., Davis J.A., 2003, Molecular-scale characterization of uranium sorption by bone apatite materials for a permeable reactive barrier demonstration, Environ. Sci. Technol. 37, 4642–4649.
10. Dimović S., Smičiklas I., Plećaš I., Antonović D., Mitrić M., 2009, Comparative study of differently treated animal bones for Co^{2+} removal. J. Hazard. Mater. 164, 279–287.
11. Bigi A., Boanini E., Capuccini C., Gazzano M., 2007, Strontium-substituted hydroxyapatite nanocrystals, Inorg. Chim. Acta 360, 1009–1016.
12. Smičiklas I., Dimović S., Šljivić M., Plećaš I., Lončar B, Mitrić M., 2010, Resource recovery of animal bones: Study on sorptive properties and mechanism for Sr^{2+} ions, J. Nucl. Mater. 400, 15–24.
13. Cha J., Cui M., Jang M., Cho S-H., Moon D.H., Khim J., 2011, Kinetic and mechanism studies of the adsorption of lead onto waste cow bone powder (WCBP) surfaces, Environ. Geochem. Health 33, 81–89.
14. Smičiklas I., Onjia A., Raičević S., Janaćković Đ., Mitrić M., 2008, Factors influencing the removal of divalent cations by hydroxyapatite, J. Hazard. Mater. 152, 876–884.
15. I. Langmuir, 1918, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40, 1361–1403.
16. H. Freundlich, 1909, Kapillarchemie, Eine Darstellung der Chemie der Kolloide und verwandter Gebiete, Akademische Verlag sgesellschaft, Leipzig.

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POSSIBILITY OF REMOVAL OF HEAVY METALS AND SELENIUM FROM WASTEWATER OF THE COPPER SMELTER PLANT, BOR USING SOLID FERRATE(VI)

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ABSTRACT

Examined was the possibility of heavy metals (Cu, As, Sb) and Se removal in synthetic wastewater from minning industry using Fe(VI) salts in solid state, environmentally friendly oxidants and coagulants. Synthetic wastewater used in the experiment was synthesized according to the composition and characteristics of real wastewater from the Copper Smelter Plant of Mining and Smelting Combine Bor. The tendency of decreasing concentrations of metals and Se in the wastewater with the amount of added ferrate(VI) has been shown. Removal of heavy metals and selenium by barium ferrate in aqueous solutions could be possible up to: 100 % for Cu, 97,18 % for As, 98,37 % for Sb and 6,06 % for Se by using ferrate(VI) in the ratio M : Fe(VI) = 1:12.

Key words: Heavy metals, selenium barium ferrate, hydrometallurgical wastewater, ICP, minning industry.

INTRODUCTION

Intensive exploitation and processing of ores leads to the degradation and pollution of the environment due to the wastewater generated in these processes. Wastewater from mining and metallurgical processes is characterized by low pH value and high concentrations of sulfates, heavy metals and some nonmetals. The heavy metals load is of greater concern than the acidity in the terms of environmental damage. Heavy metals are generally considered those whose density exceeds 5 g per cubic centimeter. Most of the elements falls into this category are highly water soluble, well-known toxics and carcinogenic agents. Heavy metals are considered to be the following elements: copper, silver, zinc, cadmium, gold, mercury, lead, chromium, iron, nickel, tin, arsenic, antimony, molybdenum, cobalt, manganese, and aluminum.

Consequence of discharge of the untreated mine wastewater in the environment are reflected in long-term contamination of soils to which mine waters come in contact and accumulation of heavy metals therein, entering of mine wastewater into surface water, and mixing of mine wastewater with ground waters. Therefore, hydrometallurgical wastewaters are among the most serious threats to the human population and the fauna and flora of the receiving water bodies [1]. Due to the high solubility in aqueous media, heavy metals can be easily absorbed and accumulated in living organisms and directly transferred to the human food chain, thus exhibiting a high health risk to consumers. Some heavy metals, even at rather low concentrations, have harmful effects on human health, and many are listed in the U.S. Environmental Protection Agency (Washington, D.C.) priority pollutant list. Table 1 provides the values of the Maximum Contaminated Level (MCL) standards, as well as the health risks of the heavy metals and selenium present in the wastewater of mining and metallurgical processes [2,3].

Table 1. The MCL standards for the most hazardous heavy metals

Heavy metal	Toxicities	MCL(mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0,05
Antimony	Cancer	0,006
Cadmium	Kidney damage, renal disorder, human carcinogen	0,02
Chromium	Headache, diarrhea, nausea, vomiting, carcinogen	0,05
Copper	Liver damage, Wilson disease, insomnia	1,0
Nikel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0,20
Zinc	Depression, lethargy, neurological signs and nervous system	5,0
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0,05
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system and nervous system	0,002
Selenium	Liver damage	0,01

Because of this, the requirements for the removal of heavy metals from hydrometallurgical wastewater are becoming stricter and it is necessary to find a method for their efficient removal below the maximum permissible concentrations.

Removal of heavy metals and selenium from wastewaters can be accomplished through various treatment options. Some of conventional treatment processes for their removal are ion exchange, chemical precipitation, various adsorption methods and membrane separation process [4,5]. However, all these methods have their drawbacks, which are reflected primarily in the insufficient level of heavy metals and selenium removal, high energy consumption and the formation of toxic products[6].

Unlike the conventional methods, ferrate(VI) show the great ability to remove heavy metals and selenium from wastewater and at the same time do not form toxic byproducts. Ferrate(VI) has a high oxidation potential (E = 2.20 V), which makes it very useful in water purification. The ferric hydroxide gel generated after ferrate(VI) decomposition could perform the adsorption and co-precipitation of metal ions in wastewater [7,8]. Dual role of ferrate(VI), which is an oxidant and a coagulant at the same time, makes this process very simple. Ferrate(VI) is thus expected to be an effective, environmentally safe and simple to use chemical for the removal of heavy metals and Se from aqueous solutions.

Problem that complicates the use of ferrate(VI) in the treatment of wastewater is a relatively complex method of chemical synthesis, which is usually applied. The process of chemical synthesis of ferrate(VI) has to be carried out under strictly controlled conditions due to the risk of explosion and poisoning. However, by using the method of electrochemical synthesis of an alkaline solution of ferrate(VI) in a two-part flow-through electrochemical cell [9,10], it is possible to obtain ferrate(VI) solution in a simple way. Since the ferrate(VI) synthesized in this way are thermodynamically unstable in aqueous solutions because they easily oxidize water and convert into Fe(III), they are suitable only for use at the production site. In order to overcome this problem and expand the area of their application there is a need for the synthesis of the solid Fe(VI) salts, such as $BaFeO_4$ which could be stable for a long time in dry atmosphere.

The objective of this paper is to investigate the effectiveness of solid ferrate(VI) salts obtained from electrochemically synthesized ferrate(VI) solution in the treatment of hydrometallurgical wastewater containing heavy metals and Se as a primary or secondary process in conventional wastewater treatment methods. This paper presents experimental results which may be useful in defining the optimum conditions of heavy metals and Se treatment by solid ferrate(VI) with the aim of lowering concentration of heavy metals and Se below the maximum permissible concentrations.

Given the fact that the treatment was done only on a laboratory scale further optimization of the applied amount of ferrate(VI) is necessary.

EXPERIMENTAL

Materials and Methods

The stock solution of synthetic hydrometallurgical wastewater used in the experiment was synthesized according to the composition and characteristics of real wastewater from the Copper Smelter Plant of Mining and Smelting Combine Bor, Table 2.

Table 2. Characteristics of real wastewater sample from the Copper Smelter Plant of Mining and Smelting Combine Bor; combined flow from the electrolytic refining process

Parameter	**Unit**	**August 2012.**
		Average
Temperature	°C	25
pH		0,1
Acid content	%	3,8
	g/dm^3	38,9
Dissolved metals		
Cu	g/dm^3	1,8
As	g/dm^3	0,1
Sb	g/dm^3	0,0008
Se	g/dm^3	0,361

Besides the heavy metals and Se, in the wastewater are present sulphate and nitrate ions (c(H_2SO_4) = 1.770 mol/dm^3 i c(HNO_3) = 0.001286 mol/dm^3).

For the stock solution synthesis of the synthetic wastewater with the same characteristics and composition as the sample of the real water the following chemicals of p.a. quality were used: $CuSO_4*5H_2O$, As_2O_3, Sb_2O_3, SeO_2, H_2SO_4 i HNO_3.

Solid barium ferrate ($BaFeO_4$) was synthesized by using previously electrochemically synthesized N_2FeO_4 alkaline solution. According to previous studies, the process of electrochemical synthesis of the N_2FeO_4 solution was based on transpassive anodic dissolution of iron alloys in a 10 M NaOH solution and it was carried out in a two-part flow-through electrochemical cell [9,10].

The synthesis of solid $BaFeO_4$ is based on the reaction of $Ba(OH)_2$ and previously synthesized N_2FeO_4, according to the reaction:

$$Na_2FeO_4 + Ba(OH)_2 \rightarrow BaFeO_4 \downarrow + 2NaOH \qquad (1)$$

Very poorly soluble $BaFeO_4$ precipitate was quantitatively separated from the solution by filtration through a sintered glass filter with the pore size of 2.0 μm. The precipitate ferrate(VI) was washed until neutral pH, dried at a slightly elevated temperature under vacuum and stored in a desiccator filled with silica gel. The SEM micrographs of the $BaFeO_4$ powder surface morphology are given in Figure 1.

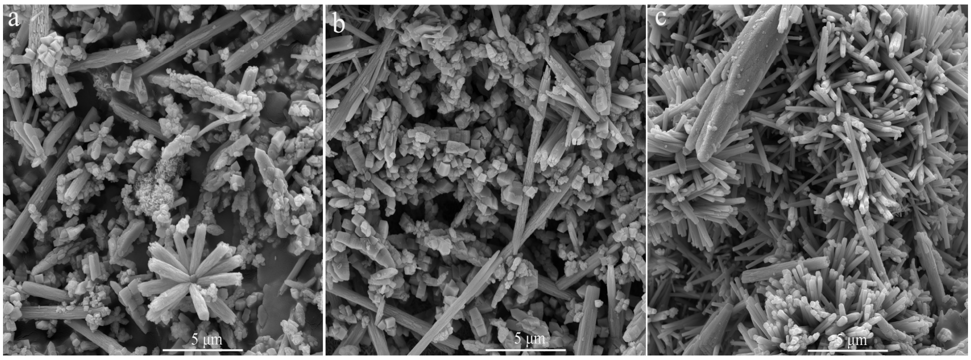

Figure 1. SEM Images of electrochemically synthesized $BaFeO_4$ powder

All chemicals used in the synthesis were prepared from analytical grade reagents and bi-distilled water.

$BaFeO_4$ yield and purity *determination* were performed by titrimetric chromite method [11]. The yield was 90 % of theoretical value with purity of 95%.

Procedure

Considering the fact that precipitation of heavy metals by hydroxides is most effective in alkaline medium, in the first stage of the treatment five 50 ml samples of the synthetic wastewater with an initial pH = 0.1 had their pH adjusted to the value of 9 by adding sodium hydroxide of p.a. quality [12]. The samples were treated at room temperature (25 ^oC), stirred for 10 minutes using the Jar test with a four-unit stirrer (Velp JLT4) at the speed of 300 rpm and for 20 minutes at the speed of 40 rpm, and then precipitated for 24 h. The treated samples were then centrifuged and filtered through a filter with the pore size of 0.20 μm.

In the second stage of the treatment, four samples from previous stage were treated by solid $BaFeO_4$ in molar ratios M : Fe(VI) = 1:2; 1:4; 1:8; 1:12, while the fifth sample remained untreated. The second stage of the treatment was carried out at room temperature (25 ^oC), stirred for 30 minutes using the Jar test with a four-unit stirrer (Velp JLT4) at the speed of 300 rpm and for 1h at the speed of 100 rpm. After 24 h of precipitation, the treated samples were filtered through a filter with the pore size of 0.20 μm.

The changes in heavy metals and Se concentrations treated by NaOH and $BaFeO_4$ were determined by analyzing the treated samples using an ICP Thermo iCAP Q device.

RESULTS AND DISCUSSION

Results of heavy metals and Se removal via precipitation by NaOH show high efficiency in Cu and Sb removal but low efficiency in the removal of As and Se, Table 3.

Table 3. Reduction of heavy metals and Se concentrations in the samples of wastewater from minning industry before and after the treatment by NaOH

Elements	**c, mg/l before treatment**	**c, mg/l after NaOH treatment**	**Removal, %**
Cu	1800	0,12	99,99
As	100	99,86	0,14
Sb	0,8	0,051	93,62
Se	361	358,43	0,71

The synthetic wastewater containing dissolved heavy metals (Cu, As, Sb) and Se treated by solid $BaFeO_4$, in various molar ratios (M : Fe(VI) = 1:2; 1:4; 1:8; 1:12) has shown a tendency of decreasing concentrations of metals and Se with increasing the amount of added ferrate(VI). Results of heavy metals and Se removal by $BaFeO_4$ from the samples of minning wastewater are shown in Table 4. pH value after the treatment was 9.

Table 4. Reduction of heavy metals and Se concentrations in the samples of wastewater from minning industry before and after the treatment by $BaFeO_4$

c($BaFeO_4$), mol/l	**M : Fe(VI)**	**pH of the samples**	**c(Cu), mg/l**	**c(As), mg/l**	**c(Sb), mg/l**	**c(Se), mg/l**
0		0	1800	100	0,8	361
0.0224	(1:2)	9	<0,05	30,19	0,029	351,32
0.0448	(1:4)	9	<0,05	5,12	0,024	344,65
0.0896	(1:8)	9	<0,05	3,34	0,017	342,50
0.1344	(1:12)	9	<0,05	2,82	0,013	339,12
Removal, %			100	97,18	98,37	6,06

Treatment results show very high efficiency in Cu removal by NaOH, 99,99% in the first step of the treatment. Therefore, further removal of Cu by $BaFeO_4$ is not necessary.

Due to law mobility of As(III) in aqueous solutions it can not be removed from the wastewater by NaOH. However, As removal by $BaFeO_4$ could be up to 97,18 % when M : Fe(VI) ratio is 1:12 because of high oxidation potential of Fe(VI) which provides As(III) oxidation to As(V). Ferrous hydroxide, formed by reduction of ferrate(VI), as a powerful coagulant removes it easily from the solution.

Antimony could be successfully removed in very high percentage (93,62 %) only by using NaOH. Higher efficiency removal of Sb was achived by $BaFeO_4$ (98,37 %).

Removal of selenium was extrimely low in the first stage of the treatment, 0,71%. After the treatment by Fe(VI), removal was more successfull (6,06 %) but yet not satisfying. Higher M : Fe(VI) ratio is needed because a large part of $BaFeO_4$ is spent on the oxidation. Further optimisation of the treatment conditions should be done in order to improve removal efficiency of selenium by $BaFeO_4$ from aqueous solutions.

CONCLUSION

Because of all advantages of $BaFeO_4$ in comparison to other conventional methods such as: simplicity, lower consumption of chemicals, non-toxic products and exceptional purity of obtained ferrate(VI) the aim of the paper was to examine the possibility of heavy metals and Se removal from hydrometallurgical wastewater by $BaFeO_4$. It has been shown that the removal of heavy metals by $BaFeO_4$ in aqueous solutions can be possible up to: 100 % for Cu, 97,18 % for As, 98,37 % for Sb, 6,06 % for Se by using ferrate(VI) in the ratio M : Fe(VI) = 1:12. By applying larger amounts of ferrate(VI) a more efficient removal of heavy metals could be reached which requires further optimization of the treatment process.

Acknowledgement

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REFERENCES

1. Babel S., Kurniawan T.A., 2004., Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. Chemosphere, 54(7): p. 951- 967.
2. THE MASSACHUSETTS ESTUARIES PROJECT, Embayment Restoration and Guidance for Implementation Strategies, 2003., Massachusetts Department of Environmental Protection
3. Babel S., Kurniawan T.A., 2003., Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazard. Mater. B97, 219–243.

4. Eccles H., 1999. Treatment of metal-contaminated wastes: why select a biological process? Trends Biotechnol. 17, 462–465.
5. Grosse, D. W., 1986., A Review of Alternative Treatment Processes for Metal Bearing Hazardous Waste Streams. J. Air Pollut. Control Assoc., 36(5), 603-614.
6. Janson, C. E.; Kenson, R. E.; Tucker, L. H., 1982, Treatment of Heavy Metals in Wastewater. Environ. Prog., I, 202-216.
7. Potts, M. E.; Churchwell, D. R., 1994., Removal of Radionuclides in Wastewater Utilizing Potassium Ferrate(VI), Water Environ. Res., 66, 107-109.
8. Murmann, R. K.; Robinson, P. R., 1974., Experiments Utilizing Ferrate Ion for Purifying Water. Water Res., 8 (1), 543-547.
9. Čekerevac M.I., Nikolić-Bujanović Lj.N., Jokić A., Simičić M.V., 2010., Investigation of electrochemical synthesis of ferrate Part II: Optimization of the process parameters, Hem. ind., 64 (2) 111-119.
10. Nikolić Bujanović Lj., Simičić M., Čekerevac M., 2012., Elektrohemijska sinteza ferata(VI) u čvrstom stanju, Hem. Ind. 66 (4) 455–460.
11. Schreyer J.M, Thompson G.W., Ockerman L.T., 1950., Oxidation of Chromium(III) with Potassium Ferrate(VI), J. Am. Chem. Soc., 22 1426-1427.
12. Peters R. W., Ku Y., Bhattacharyya D., Evaluation on recent treatment techniques for removal of heavy metals from industrial wastewaters, AlChE SYMPOSIUM SERIES

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METAL(LOID)S CONTENT IN A MEDICINAL HERB GROWN IN INDUSTRIALLY POLLUTED AREA

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ABSTRACT

This study was performed in order to investigate the potential of using nettle for biomonitoring purposes. The content of As and Cu in the samples of nettle roots, stems and leaves were assessed in three sampling terms. The area chosen for this study is known for pyrometallurgical copper production from sulphide ores. By comparing As and Cu content in nettle parts to those in soil, it was shown that nettle roots and leaves acted as excluders. Accumulation of Cu in nettle parts was observed for the specific Cu content in soil. Translocation factor indicated efficient translocation of Cu.

Key words: nettle, biomonitoring, soil pollution, As, Cu.

INTRODUCTION

Soil, besides being a growth medium for plants, also acts as a geochemical sink for contaminants [1]. Metals and metalloids (metal(loid)s) represent one of the major groups of genotoxic polluting substances in the environment, which pose a serious threat to human health, as well as environmental well–being. Although heavy metals are naturally present in soils, contamination from industry, agriculture, and combustion of fossil fuels results in increase of their prevalence [2]. One of the main topics of environmental biogeochemistry is monitoring of the pollution status of the environment using plants. Quick reactions of plants to chemical changes in the environment, as well as the fact that they may be affected by different polluting substances, have resulted in a growing interest for bioindicators [3]. According to Gjorgieva et al. [3], although some amounts of heavy metals may pass through stomata, the major heavy metal transfer occurs from roots to leaves via transpiration stream from soil water. The mechanisms for uptake and transport of essential elements (Cu for example) also provide an entrance of non–essential elements (like As). The presence of both essential and non–essential elements at excessive levels may impair plant physiology [1].

Nettle (*Urtica* spp.) is an abundant species in many environments, which has been used in ecotoxicological biomonitoring studies [1]. This plant from Urticaceae family is widely used in traditional, as well as in modern medicine [4].

The aim of this study was to investigate behaviour of nettle, grown in highly contaminated area through analysis of As and Cu content in nettle roots, stems and leaves. Also, Biological Absorption Coefficients (BAC) and Translocation Factor (TF) were calculated in order to assess information on the accumulation abilities which could be useful for biomonitoring purposes of nettle.

MATERIALS AND METHODS

The chosen study area is well known for prometallurgical copper production from sulphide ores: chalcopyrite ($CuFeS_2$), chalcozine (Cu_2S) coveline (CuS) and arsenopyrite, an iron arsenic sulfide ($FeAsS$). Sampling of soil and plant material was conducted on the Krivelj River banks in three terms: April (I term), May (II term) and June (III term). The sampling was performed at sites which were located (Figure 1): upstream from the open pit Cerovo (control, sampling site 1), near the confluence of drainage wastewaters from the open pit Cerovo (sampling site 2), along the Krivelj River before reaching the village Veliki Krivelj (sampling site 3), near the confluence of wastewaters from the open and underground pit Bor into the Krivelj River (sampling site 4), near the Krivelj River under the collector and the confluence of drainage wastewaters from the flotation tailings (sampling site 5), near the confluence of the Krivelj and Bor Rivers (sampling site 6).

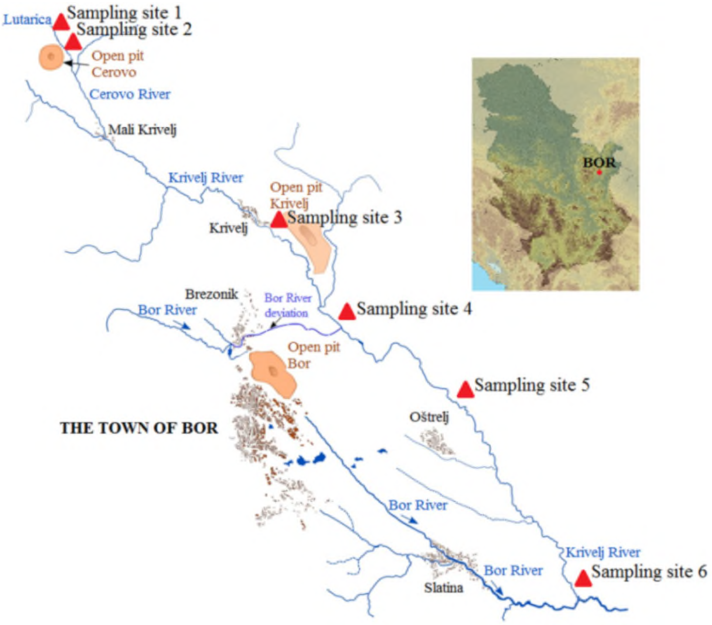

Figure 1. Location of the sampling sites along the Krivelj River banks

All chemical analysis of soil and plant material was performed in the Mining and Metallurgy Institute Bor, according to EPA standard procedures. Concentrations of As and Cu were determined by the Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP–AES, model "SpectroCiros Vision") and expressed in mg kg^{-1} dry weight (dw). The obtained concentrations for soil samples were used only for the calculation of biological factors, thus results were not shown in the paper.

RESULTS AND DISCUSSION

Plant material analysis

Although little is known of arsenic biochemical role, it is a common constituent of most plants. Passive intake of As in plants occurs with the water flow. Arsenic content in plants which are used as food, ranges from 10 to 60 μg kg^{-1} [5]. Toxic symptoms in plants, resulting from the excessive uptake of As, are leaf wilting, violet coloration, root discoloration and growth reduction [6].

Content of As in nettle parts is given in Figure 2.The average As concentrations in nettle roots and leaves from the control site (sampling site 1) amounting to 3.92 and 4.79 mg kg^{-1}, respectively, highly exceeded the range (0.5–80μg kg^{-1}) given by Kabata–Pendias [6] for plants growing in uncontaminated area. The results given by Jedynak et al. [7] for plants sampled at different distances from the gold mine showed that As content in nettle leaves did not exceed 5.3 mg kg^{-1}, which was lower than maximum As content in this study. The maximum As content in nettle roots and leaves (13.23 and 10.43 mg kg^{-1}, respectively) was higher than the data for nettle samples from industrially polluted area given by Balabanova et al. [8].

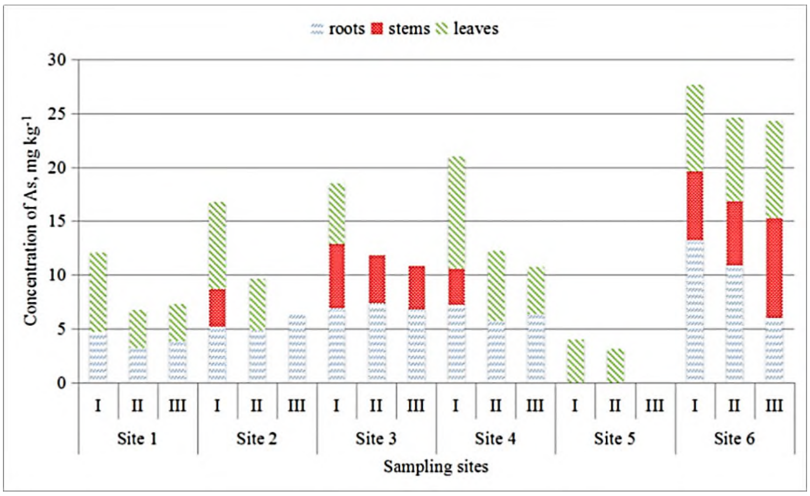

Figure 2. Arsenic content in nettle parts in three terms of sampling (Bars are missing in the case of As concentration below the LD)

Copper, an essential metal in plants, besides being a constituent of several key enzymes, also plays important functions in physiological processes (such as photosynthesis and respiration). Plants growing on soils polluted with Cu near industrial areas tend to accumulate increased amounts of this metal, especially in roots. Concentrations of Cu in whole plant shoots in the range from 20 to 100 mg kg^{-1} are usually considered to indicate the threshold of excessive content. Most common symptoms of Cu phytotoxicity are chlorosis and root malformation [6].

The Cu concentrations in roots, stems and leaves of nettle are presented in Figure 3.The average Cu content in nettle parts sampled at the control site was 87.39, 62.55 and 96.96 mg kg^{-1} for roots, stems and leaves, respectively. The maximum Cu concentrations in nettle roots, stems and leaves were 270.96, 221.83 and 249.26 mg kg^{-1}, respectively. The Cu content in nettle leaves were higher compared to the literature data given for urban, industrial and unspecified pollution [2,7,9–13]. The content of Cu in *Urtica dioica* unwashed stems, sampled from the area around lead and zinc smelter (7.16 mg kg^{-1}), given by Gjorgieva et al. [3], was lower than the data from this study (48.58–221.83 mg kg^{-1}). The Cu concentrations in nettle stems were higher compared to the data given for samples from industrial and unspecified polluted area [2,10,11]. The Cu concentrations in roots were higher than the data given for urban, industrial and unspecified pollution [9,10,13], but lower than the results for industrial and unspecified pollution [11,14].

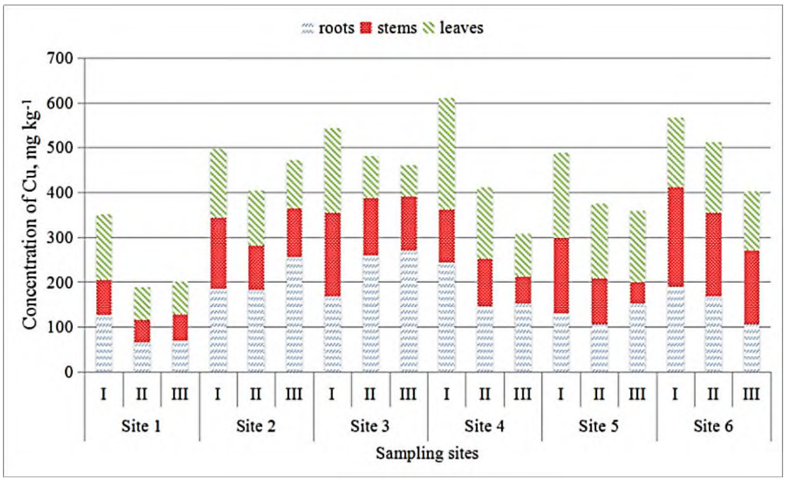

Figure 3. Cu content in nettle parts in three terms of sampling

Analysis of Biological factors

Table 1 represents calculated values of BACs and TFs for As and Cu. Biological Absorption Coefficient (BAC) was defined as the ratio of metal(loid) concentration in plant part (i.e. leaves or roots) to the corresponding metal(loid) concentration in the soil [15]. BAC, based on the ratio C_{roots}/C_{soil} represented BAC_{roots}, while BAC, based on the ratio C_{leaves}/C_{soil} represented BAC_{leaves}.

Translocation Factor (TF) represented the ratio of metal(loid) concentration in the leaves to the corresponding concentration in the roots [16]. The values of biological factors BAC and TF above 1 indicated effective accumulation and translocation of the studied metal(loid)s, respectively.

BAC_{roots} and BAC_{leaves} for As were lower than 1 at all the sampling sites in all the terms, which indicated that nettle roots and leaves acted as As excluders. BAC_{roots} and BAC_{leaves} for Cu were higher than 1 at the site 3, which may indicate that nettle roots and leaves acted as Cu accumulators at the specific Cu concentration range in soil. The site 3 was characterized with the lowest Cu content in soil. TFs for As were higher than 1 at the sites 1, 2, 4, 5 and 6, while TFs for Cu were higher than 1 at the sites 1, 3, 4, 5 and 6. The TF values higher than 1 indicated effective roots to leaves translocation of As and Cu.

Table 1. The values of BACs and TF for As and Cu

Sampling site	Term	As			Cu		
		BAC_{roots}	BAC_{leaves}	TF	BAC_{roots}	BAC_{leaves}	TF
1	I	/	/	**1.578**	0.477	0.553	**1.158**
	II	0.175	0.189	**1.077**	0.253	0.281	**1.109**
	III	0.263	0.238	0.906	0.304	0.311	**1.025**
2	I	0.039	0.062	**1.558**	0.488	0.403	0.826
	II	0.047	0.045	0.967	0.465	0.313	0.673
	III	0.278	< 0.133	< 0.478	0.847	0.350	0.413
3	I	0.563	0.460	0.817	**1.121**	**1.251**	**1.116**
	II	0.589	< 0.238	< 0.404	**1.445**	0.521	0.361
	III	0.627	< 0.275	< 0.439	**1.303**	0.332	0.255
4	I	0.303	0.436	**1.443**	0.326	0.332	**1.020**
	II	0.286	0.323	**1.131**	0.123	0.134	**1.090**
	III	0.410	0.283	0.691	0.071	0.045	0.629
5	I	< 0.313	0.416	> **1.330**	0.396	0.576	**1.456**
	II	< 0.319	0.338	> **1.060**	0.262	0.410	**1.568**
	III	< 0.326	< 0.326	–	0.283	0.296	**1.048**
6	I	0.155	0.095	0.614	0.314	0.257	0.819
	II	0.224	0.159	0.711	0.368	0.346	0.940
	III	0.171	0.252	**1.478**	0.256	0.315	**1.234**

/ Missing data for soil As concentration; – Both concentrations were lower than the LD for As; Values higher than 1 are shown in bold; Values with the < and > signs were obtained when missing As concentration was replaced with the LD for As.

CONCLUSION

Nettle part samples collected from the Krivelj River banks in three different terms, in which arsenic was detected contained toxic concentrations of this metalloid, while Cu concentrations in the nettle parts, exceeded toxic threshold concentrations, except at the control site. The analysis of Biological Absorption Coefficients for roots and leaves, revealed that nettle roots and leaves acted as excluders of As and Cu. The accumulating abilities of nettle parts, particularly roots, were found for the specific concentration range of Cu in soil (150–208 mg kg^{-1}). The obtained values of Translocation Factor for As and Cu indicated efficient translocation of these elements from roots to leaves.

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REFERENCES

1. Boshoff M., De Jonge M., Scheifler R., et al., 2014, Predicting As, Cd, Cu, Pb and Zn levels in grasses (*Agrostis* sp. and *Poa* sp.) and stinging nettle (*Urtica dioica*) applying soil–plant transfer models, Science of the Total Environment 493, 862–871, Elsevier, Amsterdam.
2. Gjorgieva D., Kadifkova Panovska T., et al., 2013, Influence of heavy metal stress on antioxidant status and DNA damage in *Urtica dioica*, 1–6, BioMed Research International, Hindawi Publishing Corporation, London.
3. Gjorgieva D., Kadifkova–Panovska T., Bačeva K., et al., 2011, Assessment of heavy metal pollution in Republic of Macedonia using a plant assay, Archives of Environmental Contamination Toxicology, 60, 233–240, Springer–Verlag, Berlin.
4. Najafipour F., Rahimi A., Mobaseri M., et al., 2014, Therapeutic effects of stinging nettle (*Urtica dioica*) in women with hyperandrogenism, International Journal of Current Research and Academic Review, 2(7), 153–160,Excellent Publishers, Tamilnadu.
5. Kabata–Pendias A., Mukherjee A., 2007, Trace elements from soil to human, Springer–Verlag, Berlin.
6. Kabata–Pendias A., 2011, Trace elements in soils and plants, CRC Press, Boca Raton.
7. Jedynak Ł., Kowalska J., Leporowska A., 2012, Arsenic uptake and phytochelatin synthesis by plants from two arsenic–contaminated sites in Poland, Polish Journal of Environmental Studies, 6, 1629–1633, HARD Pub. Co., Olsztyn.
8. Balabanova B., Stafilov T., Bačeva K., 2015, Bioavailability and bioaccumulation characterization of essential and heavy metals contents in *R. acetosa*, *S. oleracea* and *U. dioica* from copper polluted and referent areas, Journal of Environmental Health Science &Engineering, 13, 2, BioMed Central, London.
9. Kowol J., Paukszto A., Kwapuliński J., et al., 2009, Medicinal plants and their sites by metal contamination in the area of the "umbrella effect" as exemplified by Łagisza power station (Silesia, Poland), Fresenius Environmental Bulletin, 18(7), 1094–1099, Technische Unviversitat Munchen, Munich.

10. Paukszto A., Kowol J., Kwapuliński J.,et al.,2009, The usefulness of *Urtica dioica* L. in Podhale region (Poland) as herbal material in the aspect of accumulation of chosen metals, Fresenius Environmental Bulletin, 18(10), 1946–1949, Technische Unviversitat Munchen, Munich.
11. Spongberg A., Hartley L., Neher D, et al., 2008, Fate of heavy metal contaminants in a former sewage treatment Lagoon, Hancock county, Ohio, Soil & Sediment Contamination, 17, 619–629, Taylor & Francis Group, LLC, Abingdon.
12. Notten M.,Oosthoek A., Rozema J., et al., 2006, Heavy metal pollution affects consumption and reproduction of the landsnail *Cepaea nemoralis* fed on naturally polluted *Urtica dioica* leaves, Ecotoxicology, 15, 295–304, Springer, Berlin.
13. Malizia D., Giuliano A., Ortaggi G., Masotti A., 2012, Common plants as alternative analytical tools to monitor heavy metals in soil, Chemistry Central Journal, 6(Suppl 2), S6, SpringerOpen, London.
14. Tack F., Verloo M., 1996, Metal contents in stinging nettle (*Urtica dioica* L.) as affected by soil characteristics, The Science of the Total Environment 192, 31–39, Elsevier Science B.V., Amterdam.
15. Zhuang P., Yang Q., Wang H., et al., 2007, Phytoextraction of heavy metals by eight plant species in the field. Water, Air, and Soil Pollution,184, 235–242, Springer International Publishing, Cham.
16. Marchiol L., Fellet G., Boscutti F., et al., 2013, Gentle remediation at the former "Pertusola Sud" zinc smelter: Evaluation of native species for phytoremediation purposes, Ecological Engineering 53, 343–353, Elsevier B.V, Amsterdam.

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SEM AND EDS INVESTIGATION OF Zn-Sn ALLOYS AS POTENTIAL HIGH TEMPERATURE LEAD-FREE SOLDER

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ABSTRACT

In this paper two lead-free alloys have been investigated. New guidelines propose the Zn-Sn system as one of the possibilities for solder use. The investigation started with the melting of pure metals with appropriate ratios in the electric furnace and the casting of alloys. Mechanical properties were determined by measuring the microhardness of pure metals and Sn-30 mas.% Zn and Sn-70 mas.% Zn alloys. Electrical conductivity measurement was performed by direct measurement. SEM and EDS investigations were performed on pure metals as well as on the investigated alloys. The methods applied provided the quantitative information about phases present in the microstructures.

Key words: lead-free solders, Tin-Zinc alloys, microhardness, electrical conductivity, SEM/EDS analysis.

INTRODUCTION

Pb-Sn alloys have been used in die attach bonding as high temperature solders. High contents of Pb in these solders make them undergo RoHS restrictions, so a great deal of attention is given to the development of the lead-free solders [1-3].

New guidelines were proposed for high temperature lead-free solders [4]. These guidelines propose the Zn-Sn system as one of the possibilities, because they do not form any IMCs (massive intermetallic compounds) over any range of temperature and composition [5]. Investigation of said alloys must be performed in order to see if they exhibit good mechanical and electrical properties.

To further investigate this system, the chemical composition of the alloy was changed in order to investigate the unusual percent of Zn in the alloy. Besides that, in this paper, pure zinc and tin were investigated also as starting and ending points for comparison.

MATERIALS AND EXPERIMENTAL

Experimenting began by weighing the pure metals and preparing the charge of defined ratios for the alloys. Melting was performed in an electric furnace. Samples were cast in graphite mold and then cut into appropriate dimensions.

The investigation started by measuring the microhardness of pure metals and alloys. Vickers microhardness was measured on PMT-3 microhardness tester with a 50 gf load.

Physical properties were determined by measuring the electrical conductivity. Electrical conductivity values were measured using Sigmatest 2.063 conductivity tester. Microhardness and electrical conductivity values were presented as the arithmetical values of all three measurements.

Microstructures of investigated samples were observed using a scanning electron microscope Tescan Vega 3 LMU with installed EDS detector on polished samples unetched or etched with appropriate solutions. Samples were recorded at different magnification.

The alloy compositions were chosen in accordance to Sn-Zn phase diagram. The alloys are presented on Figure 1 [6].

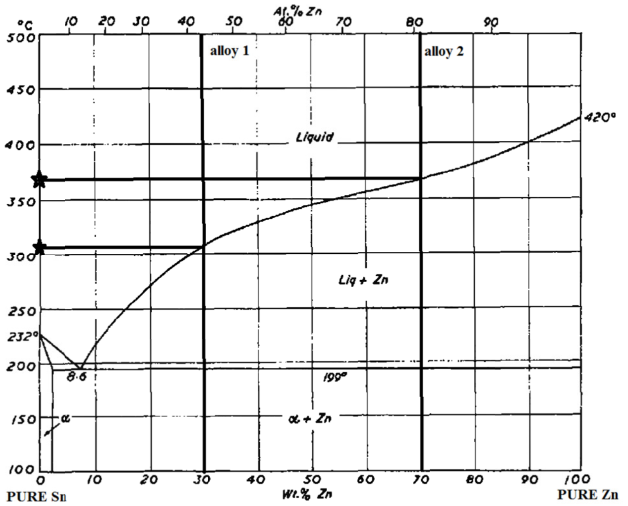

Figure 1. Tin-Zinc phase diagram [6]

RESULTS AND DISCUSSION

Table 1 shows the results of the microhardness and electrical conductivity measurements. It can be concluded that with the increment of zinc in the alloy composition, the mechanical and electrical properties increase.

Table 1. Microhardness and electrical conductivity of investigated samples

Sample type	Microhardness [$HV_{0.05}$]	Electrical conductivity [%IACS]
Pure Zn	130	25.5
Zn-30Sn	36.54	21.9
Sn-30Zn	21.56	16.7
Pure Sn	11.97	14.1

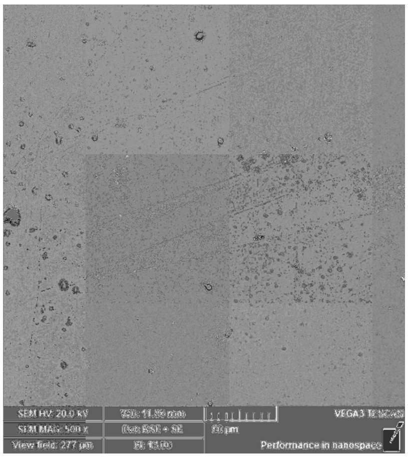

Figure 2a. Microstructure of Zn etched with 2% Nital (mag. x500)

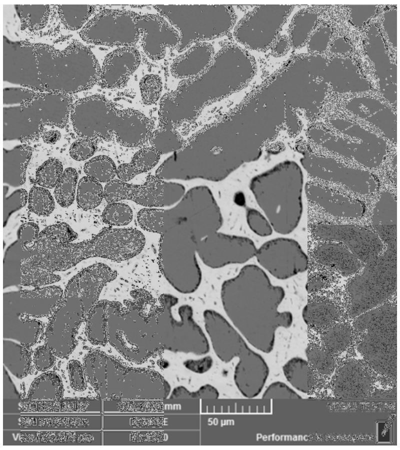

Figure 2b. Microstructure of Zn-30Sn etched with HCl in C_2H_5OH (mag. x500)

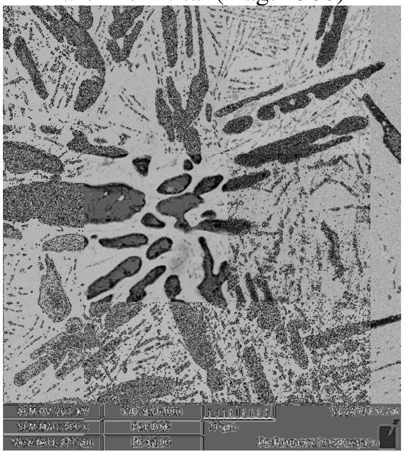

Figure 2c. Microstructure of Sn-30Zn unetched (mag. x500)

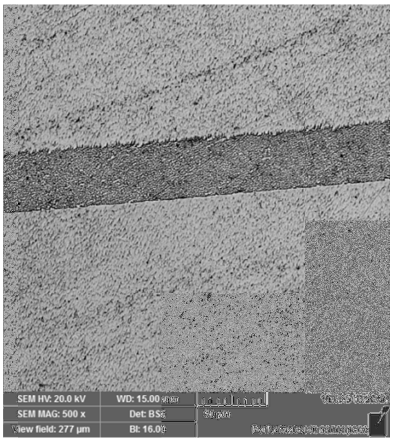

Figure 2d. Microstructure of Sn etched with HCl in C_2H_5OH (mag. x500)

Figures 2a-d show the characteristic tin, zinc and alloy microstructures. Zinc microstructure is composed of rich Zn needle-like particles imbedded in Zn base. Those needle-like particles are present in both investigated alloys, but in different quantities.

Zn-rich globules, spheroids can hinder the dislocation movement causing an increment in mechanical properties due to a hardening effect [7]. Needle-like shaped Zn-rich phase distributed in the eutectic mixture can lower mechanical properties because movement of dislocation across the lattice is easier as Garcia et. al suggested [8].

Looking at the results presented in Table 1, it can be seen that the value of zinc is about twice as high as that of tin. So it is logical that the electrical conductivity increases with the addition of zinc in the alloys' compositions.

More in-depth analysis was performed on the samples, including SEM and EDS investigation at higher magnification. Figures 3a and 3b show the microstructures of investigated alloys, with EDS analysis given in tables 2a and 2b.

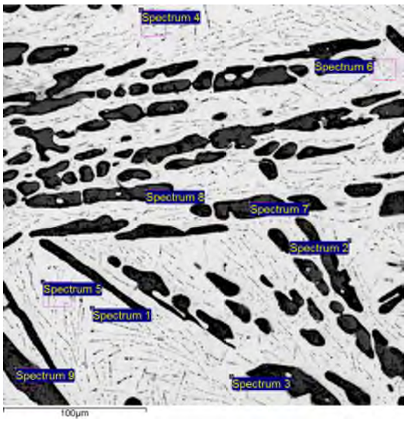

Figure 3a. Microstructure of Sn-30Zn alloy, with marked spectrums (mag. x1000)

Table 2a. EDS analysis of the Sn-30Zn alloy, given in atomic %

Spectrum	Zn	Sn
Spectrum 1	2.52	97.48
Spectrum 2	1.34	98.66
Spectrum 3	4.13	95.87
Spectrum 4	4.51	95.49
Spectrum 5	4.42	95.58
Spectrum 6	5.59	94.41
Spectrum 7	100.00	
Spectrum 8	100.00	
Spectrum 9	98.91	1.09

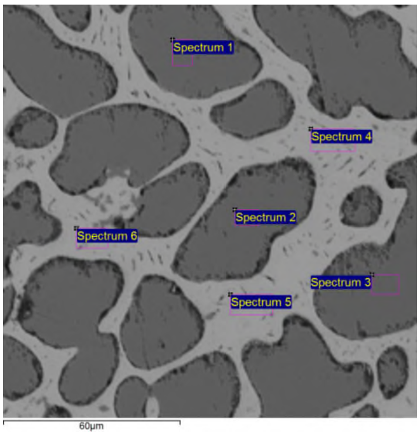

Figure 3b. Microstructure of Zn-30Sn alloy, with marked spectrums (mag. x2000)

Table 2b. EDS analysis of the Zn-30Sn alloy, given in atomic %

Spectrum	Zn	Sn
Spectrum 1	100.00	
Spectrum 2	100.00	
Spectrum 3	100.00	
Spectrum 4	8.81	91.19
Spectrum 5	7.15	92.85
Spectrum 6	18.14	81.86

The microstructure of the presented figures consists of primary bright and dark colour phases. The phase that appears white is the eutectic mixture of β-Sn/α-Zn. Zn platelets that appear dark in colour are surrounded by eutectic β-Sn/α-Zn phases as seen on figures 2c and 3a. EDS analysis revealed that the eutectic mixture consists of around Sn-8.8Zn, which is in agreement with the phase diagram and literature data [5]. If the Zn content increases the zinc platelets are less common in the eutectic mixture relative to the primary α-Zn phase.

CONCLUSIONS

- This paper provided an experimental investigation of two alloys with different Sn/Zn ratios as well as an investigation of the pure metals.
- Metallographic investigation shows the typical eutectic structures with limited solubility between Zn and Sn. Zn appears as needle shaped when pure to plate-like in the eutectic mixture. Also, α-Zn globules are present with high Zn content. Tin appears as a clear primary α-phase and presents in the form of β-Sn/α-Zn eutectic mixture.
- Microhardness investigation shows the increment of mechanical properties due to appearance of the different Zn phases. A hardening effect of said phases can be expected depending on their morphology and homogeneity.
- The obtained values of electrical conductivity show increment with the addition of zinc. Zinc is more conductive than tin, and the increment is to be expected. Finely dispersed phases based on zinc can probably cause easier movement of the electrons causing the increment of electrical conductivity.

REFERENCES

1. Kim K. S., Yu C. H., Kim N. H., Kim N. K., Chang H. J., Chang E. G., Isothermal aging characteristics of Sn–Pb micro solder bumps, Microelectronics Reliability 43 (2003), 757–763.
2. Zhuang W. D., Chang P. C., Chou F. Y., R. K., Effect of solder creep on the reliability of large area die attachment, Microelectronics Reliability 41 (2001), 2011–2021.
3. Nagatomo Y., Nagase T., Shimamura S., FEM Analysis of Thermal Cycle Properties of the Substrates for Power Modules, Journal of The Japan Institute of Electronics Packaging 3 (2000), 330–334.

4. Lee J. E., Kim K. S., Suganuma K., Takenaka J., Hagio K., Interfacial Properties of Zn-Sn Alloys as High Temperature Lead-Free Solder on Cu Substrate, Materials Transactions 46 (2005), 2413–2418.
5. Lee J., Kim K., Suganuma K., Inoue M., Izuta G., Thermal Properties and Phase Stability of Zn-Sn and Zn-In Alloys as High Temperature Lead-Free Solder, Materials Transactions 48 3 (2007), 584-593.
6. Brandes E. A., Brook G. B., Smithells Metals Reference Book 7th edition, Butterworth-Heinemann, Woburn, 1992.
7. Garcia L. R., Osorio W. R., Piexoto L. C., Garcia A., Mechanical properties of Sn–Zn lead-free solder alloys based on the microstructure array, Materials Characterization 61 (2) (2010), 212–220.
8. Garcia L. R., Peixoto L. C., Osorio W. R., Garcia A., Globular-to-needle Zn-rich phase transition during transient solidification of a eutectic Sn–9%Zn solder alloy, Materials Letters 63 (2009), 1314–6.

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OVERVIEW OF GASIFICATION METHODS FOR LOW QUALITY COAL AND WASTE

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ABSTRACT

The article presents an overview of typical solutions of gasifiers that can be used for the gasification of low quality coal or coal waste slurries. Recent data on the gasification by application and number of gasifiers by primary feedstock is given. A brief summary of advantages and drawbacks of each type of gasifier is given and one technology is described in more detail. It appears that modern gasifiers are capable of handling low quality feedstock such as coal waste slurries or biomass.

Key words: gasification, coal waste slurries, gasifiers.

INTRODUCTION

Coal gasification is considered as one of the Clean Coal Technologies since it reduces the environmental impact of coal as a feedstock for energy production. In comparison to conventional coal combustion methods the emissions of solid particles, NO_x and SO_x are significantly reduced. With the ability to capture CO_2, coal gasification methods are considered as one of the most promising technologies that can reduce greenhouse gas emissions without the drastic switch to other fuel. Additional benefits in using gasification technology is its fuel flexibility where both coal, coal slurries or biomass can be gasified.

The gasification technology is known since the beginning of the XIX century when the Lurgi patented its first gasifier in 1887. It was the first application of gasification to supply syngas for lightning and heating. In the 30-ties of XX century the technology was developed and was commercially used for fuel conversion, since that time the interest in the gasification technology decreased due to low prices of natural gas. When the fuel crisis in the 70-ties caused drastic increase in natural gas and oil prices interest in the gasification technologies and fuel conversion raised. Since that period many new technologies have been developed and implemented in the petrochemical industry mainly for the production of ammonia, methanol and hydrogen from the syngas. In general, gasification process (a thermo-chemical process) breaks down coal - or virtually any carbon-based feedstock - into its basic chemical constituents. This is achieved by reacting the material at high temperatures (>700°C) without combustion and with carefully controlled amount of oxygen and/or steam. Under these conditions, molecules in coal break apart, initiating chemical reactions that typically produce a mixture of carbon monoxide, hydrogen and other gaseous compounds.

There are currently 74 plants under construction worldwide that will have a total of 238 gasifiers and produce 83 MWth. Gasification for chemicals has been, and probably will remain, the most important gasification application for the foreseeable future. A recent study shows that about 25% of the world's ammonia and over 30% of the world's methanol are now being produced via gasification (as compared to 10 % in each case ten years ago), see Fig. 1. Coal is now the dominant feedstock (Fig. 2) and will continue to be so for the foreseeable future. There are still gasification plants using oil as a feedstock, but that number has dropped considerably as the price of crude oil has increased. The figure for gas feedstock plants consists largely two "gas to liquids or GTL" plants-Bintulu and Pearl [1].

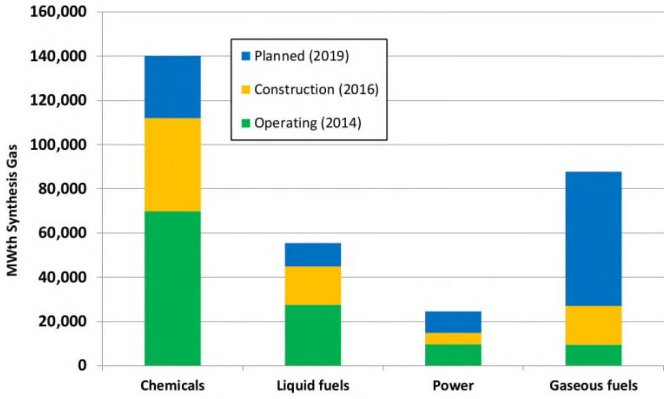

Figure 1. Gasification by application [2]

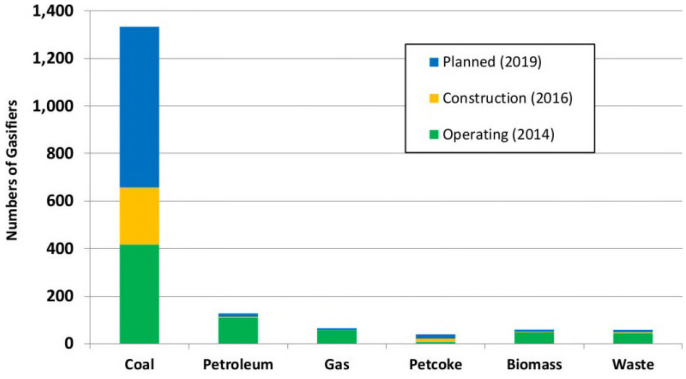

Figure 2. Number of gasifiers by primary feedstock [2]

Gasification for liquid and gaseous fuels is becoming increasingly important. While the demand for transportation fuels (particularly gasoline) has declined in the United States, the demand has been increasingly sharply in other parts of the world, primarily Asia. Benefits of using gasification are particularly important in case of low quality coals or coal waste where carbon content is too low to be used in conventional combustion technologies. In this article an overview of typical gasifiers for low quality coal or coal slurry gasification are presented and described.

GASIFIER TYPES

There are three common types of gasifiers used in commercially available gasification systems: fixed-bed, fluidized bed and entrained flow. There is also one technology called Molten-bath capable of gasification both coking and non-coking coals but its development is not yet mature enough to be considered for wide application. Comparison of the most popular commercially available gasifiers is shown in Table 1. Entrained-flow gasifiers are the most common commercial gasifier due its high throughput when compared to the other technologies currently available in the market.

Table 1. Most common, commercially available gasifiers for solid fuels [2]

Gasifier type	**Advantages**	**Disadvantages**	**Commercial examples**	
Fixed-bed	Less oxidant, low gas residence time simple construction, low pressure drop, high carbon conversion	High solid residence time, high methane content, poor temperature distribution control, caking coal issues	**Lurgi slagging gasifier**	
			Combustion zone T (°C)	1260–1370
			Residence time	10–15 min
			Lurgi dry ash gasifier	
			Gasification zone T (°C)	620–815
			Combustion zone T (°C)	980–1370
			Residence time	1 h
			Wellman-Galusha gasifier	
			Combustion zone T (°C)	1315
			Residence time	4 h
Fluidized-bed	Moderate reaction rate, moderate residence time for solid and gas, good mixing, good temperature distribution control, moderate oxygen/steam demand	No vitreous ash produced, moderate energy demand, higher pressure drop	**Battelle ash agglomerating gasifier**	
			Gasification zone T (°C)	870–980
			Combustion zone T (°C)	1100–1150
			Residence time	-
			Synthane gasifier	
			Gasification zone T (°C)	815–980
			Residence time	–
			Winkler gasifier	
			Gasification zone T (°C)	980–1150
			Residence time	20–30 min
			U-Gas	
			Gasification zone T (°C)	840–1100
			Residence time	–
Entrained-flow	Less technical complexity, suitable	Large oxidant requirement, high	**Koppers-Totzek gasifier**	
			T (°C)	Max 1900

	for all coal types, very short residence time (seconds or less)	temperature, slagging operation	Residence time	Less than 1 s
			GE gasifier	
			Gasification zone T (°C)	1200–1480
			Residence time	3 s
			Shell coal gasifier	
			Flame T (°C)	1800–2000
			Residence time	0.5–4 s
			Aerojet Rocketdyne	
			Outlet T (°C)	1297–1926
			Flat-flame T (°C)	3200
			Residence time	0.2–0.5 s
			Chicago Bridge & Iron E-STR	
			First stage T (°C)	1316–1427
			Second stage T (°C)	1010
			Residence time	–
			Siemens Gasifier	
			Gasification zone T (°C)	1300–1800
			Residence time	–
Molten-bath	Capable of both caking/non caking coals	High oxidation rate, carryover of alkalis, complicated regeneration system	**Rockwell gasifier**	
			Effluent gas T (°C)	980
			Melt bed T (°C)	980
			Residence time	–

GASIFIERS FOR LOW QUALITY COAL

Low quality fuels have high ash content and usually high moisture content. Increased moisture content requires more energy to vaporize the water and increased ash content means a greater mass flow of inerts which must be heated up. Therefore, both increased moisture and ash content have the effect of higher oxygen consumption and lower cold gas efficiency. Ash properties are of great importance in gasification process and this is particularly important in low quality fuels. Mineral matter and/or inorganic components may vaporize, form liquids or solids. Formation of three phase products is a significant difference to the coal burning process. The major problem in the process of gasification is the condensation of inorganic compounds which may result in slagging. Slag is formed when ash particles deposit on the gasifier wall and flow down as highly vitreous product. To some extent slagging effect is desirable in entrained-flow gasifiers since a small slag layer on the refractory is desirable, as this layer protects the refractory lining and reduces heat loss. However at high temperature and reduced viscosity, the molten slag layer can be very corrosive and can penetrate into the air-cooled refractory lining. Technology particularly suited for low quality coal or other low quality fuel combustion is the SGT technology by the SYNTHESIS ENERGY SYSTEMS, INC. company [3]. This technology uses bubbling fluidized bed reactor and gasification temperature ranges from 840^{0}C to 1.100^{0}C which is much below vitrification point of ash for typical low quality coals. The product of gasification is the syngas which can be used as the basis or production of chemicals or fuels. Properties of the fuels for the SGT gasifier are shown in Table 2.

Table 2. Parameters of fuel for SGT gasification technology

Moisture [%]	1 – 41
Volatile matter [%]	3 – 69
Carbon content [%]	6 – 83
Sulphur [%]	0,2 – 4,6
Free swelling index	0 – 8
Ash content [%]	<1 – 55
Ash melting point [°C]	1.038 – 1.371
Heat of combustion [kJ/kg]	12.791 – 32.558

It is worth mentioning that pollutants such as mercury, cadmium, etc. are recovered during the process of gasification. The mineral matter transforms into ash with 1% carbon content which can be used further as the input in the cement industry or for production of construction materials. It is worth mentioning that the requirements for the fuel in the SGT technology are suitable for coal waste slurries which are widely available and are deposited in surface impoundments particularly in southern Poland [4].

CONCLUSIONS

Examples of recently developed coal gasification technologies are not only suitable for high quality coals with low ash content but are also for coal waste slurries or biomass. In particular, fluidized bed and entrained-flow gasifiers are capable of handling high ash content fuels since the residence time necessary for the gasification is relatively short. SGT gasification technology with few existing installations can be considered as a good alternative for other utilization and recycling paths regarding the coal waste slurries.

REFERENCES

1. http://www.gasification-syngas.org/resources/the-gasification-industry/
2. M. Hossein Sahraei, David McCalden, Robin Hughes, L.A. Ricardez-Sandoval, A survey on current advanced IGCC power plant technologies, sensors and control systems, Fuel, Volume 137, 1 December 2014, Pages 245-259, ISSN 0016-2361, https://doi.org/10.1016/j.fuel.2014.07.086.
3. SYNTHESIS ENERGY SYSTEMS, INC., USA – company information
4. Lutynski, A., Lutynski, M. Assessment of coal slurry deposits energetic potential and possible utilization paths (2014) Physicochemical Problems of Mineral Processing, 50 (1), pp. 159-168

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MICROORGANISM ACTIVITY IN MINE SOILS OF BLACK LOCUST (*Robinia pseudoacacia* L.) STANDS ON COPPER MINE WASTES IN BOR, SERBIA

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ABSTRACT

Soil microorganisms represent one of the indicators of the ecosystem development and reclamation success in the revegetated mine waste areas. This research aims to evaluate microbiological activity in the surface layers under the black locust stands on copper mine wastes in Bor, and to determine contribution of the main physiological groups of microorganisms in organic matter turnover.

Key words: microorganisms, organic matter, mine soil, Bor.

INTRODUCTION

The development of plant life depends on the effective fertility of the soil, conditioned by the content of the organic matter and the activity of soil micro-fauna [8]. Soil microorganisms significantly contribute to the maintenance of the matter and energy flows in terrestrial environment by promoting organic matter turnover and nutrient cycling through their metabolic functioning [9]. Soil microorganism quantity and diversity is beneficial for plant growth in mine waste areas and can be used in evaluation of the primary ecosystem development or reclamation success in the mine waste areas. Speed and dynamics of soil processes depends on the amount and properties of organic matter produced by the plants, which represents the primary energetic material for soil microorganisms. Therefore, the quantity of microorganisms in the soil depends also on the content of the organic matter [7]. Decomposition of organic matter is a biological process, whose speed is largely determined by presence of soil microorganisms. Successive decomposition of dead material and modified organic matter results in the formation of humus [1].

Mine waste character and type influence the processes of mineralization and the formation of organic matter. When the biological processes start to take place in technogenic substrates, pedogenesis occures. Mineralogical composition of mine wastes causes differences in the number of soil microorganisms, respresenting the more influential factor than the soil texture (Resulić, 1997). Plant-soil biota feedback accounted for more importance then abiotic factors in natural sucession at some post-industrial habitats [3].

The aim of this paper is to determine the microbiological activity of the mine waste piles and flotation tailings under the black locust stands in copper mine wastes in Bor, and therefore evaluate their effectiveness in organic matter decomposition and synthesis of humus.

MATERIALS AND METHODS

Site characteristic

Mine waste area in Bor ($44^0$04`25``N, $22^0$05`26``E, East Serbia) consists of two main waste types resulted from the copper ore exploitation and processing: flotation tailings and overburden piles (Figure 1), covering a total area of about 150 ha. Flotation tailings consist of milled rock left after the proces of ore separation. The mine waste piles mainly consist of andesite and dacite waste rocks displaced without industrial processing. Mine waste piles and flotation tailings were partially revegetated with alochtonous tree black locust (*Robinia pseudoacacia* L.) during the period 1982–1986., with limited success [4]. Flotation tailings were covered with topsoil layer of 30 cm prior to revegetation. Total of 8 revegetated fields (4 on mine waste piles and 4 on flotation tailings) under black locust were selected for the investigation (Figure 1).

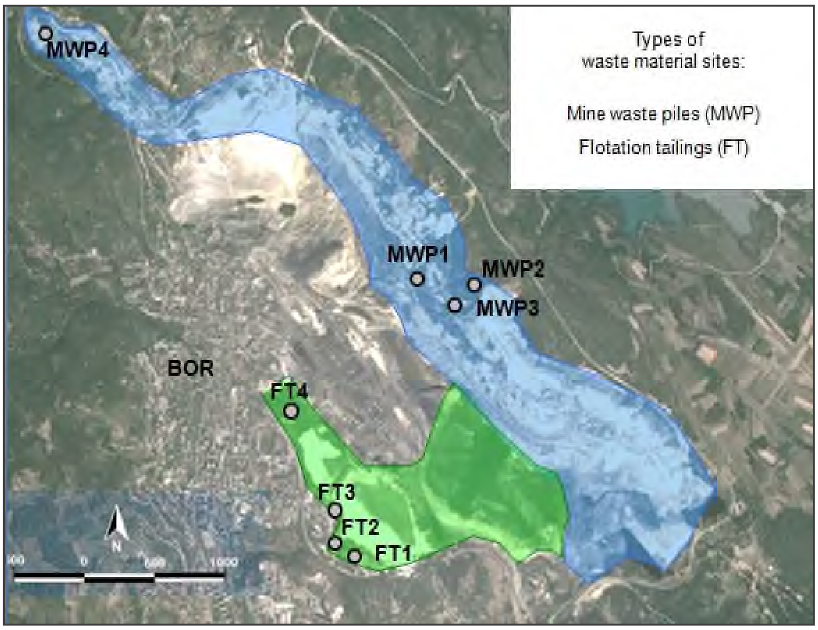

Figure 1. Mine waste sites revegetated with black locust in Bor copper mine waste area

Microorganism sampling and analysis

Mine soil from the surface horizon layer was taken with sterile spatula in spring and autumn season at all selected mine waste sites. The number of microorganisms was determined by the plate dillution method. Diluted soil suspension is introduced into adequate selective media for each physiological group. Following physiological groups of microorganisms were determined: the number of ammonifiers on meso-peptonic agar; the number of oligonitrofiles on Esbhi's agar; the number of actinomyces on synthetic agar; the number of fungi on Čapek's agar; the total number of microorganisms (total microbial content) on soil agar. Nutrient media were sown by soil suspension 0.1 ccm in 10^{-3} dilution. The media were sterilized in an autoclave at the temperature of 120ºC and transferred to petri dishes. The sowing was repeated three times and petri dishes were placed in a thermostat at the temperature of 22ºC. The determination of the total number of fungi, bacteria and actinomyces, developed on nutrient media, was performed after 7 and 14 days. The number of microorganisms was calculated as the average in thousand per 1g of absolutely dry soil.

Data analysis

Non-parametric *Spearman* rank *correlation* was used to test the association between ranked variables. Non-parametric Mann-Whitney U-test was used in order to compare means of physiological groups of microorganisms for spring and autumn seasons. All analysis were performed in Statistica 8.0. Statsoft software.

RESULTS

The average number of soil microorganisms in mine soils of black locust stands at flotation tailings and mine waste piles is presented in Figure 2.

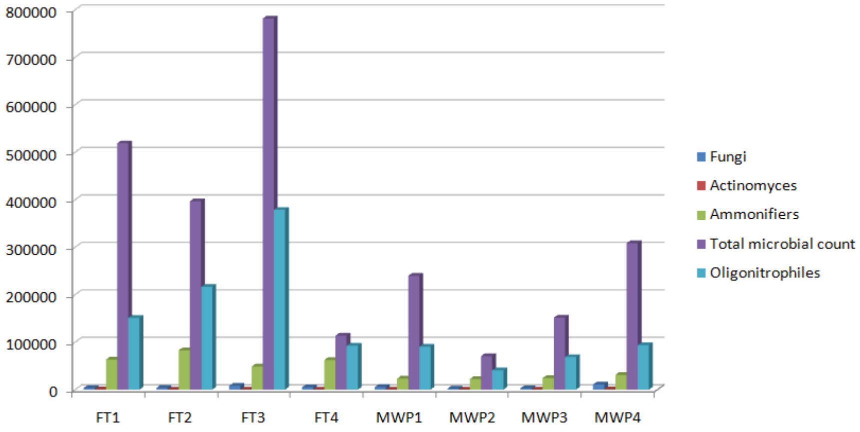

Figure 2. Average number of soil microorganism groups in black locust stands on flotation tailings (FT 1-4) and mine waste piles (MWP 1-4) in Bor

As visible in Figure 2, total content of microorganisms dominates at all investigated black locust sites, especially at flotation tailings sites (FT1-FT3). Number of oligonitrophiles follows the same trend. Average content of ammonifiers is also higher in flotation tailings sites (FT1-FT4). Lowest content or even total absence from surface soil layers of investigated sites is noticed for the physiological group of actinomyces.

Content of main physiological groups of microorganisms in spring and autumn season is reported in Table 1. Number of fungi, actinomyces, oligonitrophiles and total microbes on investigated sites varies among seasons, while number of ammonifiers show lower values for the autumn season.

Table 1. Number of microorganism physiological groups in spring and autumn season on Bor flotation tailings and mine waste piles revegetated with black locust

Group	Season	FT 1	FT 2	FT 3	FT 4	MW P 1	MW P 2	MW P 3	MW P 4
Fungi	spring	3774	1989	9163	5243	4712	2790	3747	8955
	autumn	3174	5475	6864	4746	6292	1616	1717	12554
Actinomyces	spring	1153	0	0	107	0	0	0	52.5
	autumn	113	0	0	116	0	0	0	1315
Ammonifiers	spring	79679	117267	72284	99503	29317	33265	41748	41106
	autumn	46929	48725	24854	25117	17129	11313	7189	21136
Oligonitrophiles	spring	45815	175900	671937	88804	71197	54727	78144	71893
	autumn	256181	257312	85214	96071	109529	26935	59015	115362
Total microbial count	spring	430893	299449	1262427	155140	68056	121257	229079	226381
	autumn	606447	494093	300615	72459	411317	19932	74037	390569

DISCUSSION

Mann-Whithey U-test showed statistically significant differences between the number of amonificators in spring and autumn season for the flotation tailings and mine waste piles sites (Z=2.3, p=0.02). The other groups of soil microorganisms didn`t exibit significant differences in their number between spring and autumn season at the investigated groups of sites.

On the investigated fields of Bor mine wastes (flotation tailings and mine waste pills) under black locus stands the total microbial content of soil was the most abundant in both seasons. Their higher content during the autumn season is a result of the increased presence of the end-products of decomposed organic matter, that consists of the mineral form of plant asimilatives released from soil organic layer during the year. Total microbial content of soil indicates nutritional value of the environment, but at the same time these microorganisms are the competitors to the vegetation as they use the same form of assimilatives as higher plants for their metabolic processes [2].

Total micobial content prevails over the number of ammonifiers in both seasons on all fields, indicating the decomposition of the majority of organic materials to their end-products. Plant asimilatives are therefore predominantly in the mineral form, and the synthesis of humus from the inter-products of organic matter decomposition is slow. Greater abundance of oligonitrophiles in relation to ammonifiers indicates that the synthesis of low molecular weight fraction of humic substances (fulvic acids) is ongoing, but according to a relatively high total number of microorganisms in relation to these two groups it can be concluded that the nature of the synthesized humic substances is not aggressive. The large number of ammonifiers on all investigated fields during the spring season is a result of fresh organic matter load, which presents a suitable material for these organisms. This is reflected in positive correlation ($\rho=0.67$) of their number with the content of organic matter at investigated sites. Content of ammonifiers in both seasons also positively correlates with total nitrogen content ($\rho=0.8$ in spring season, $\rho=0.68$ in autumn season).

Actinomyces actively tranform organic matter in later stages of it`s decomposition [10]. Small number or total absence of actinomyces in the investigated fields of Bor mine wastes indicates that either there is no decomposition of humic material to the end-products, or that the process is very slow. Fungi prevails over the actinomyces at all investigated sites, and have dominant role in decomposition of organic matter. Fungi exibit inverse correlation with mine soil pH ($\rho=-0.64$ in spring season, $\rho=-0.82$ in autumn season) and organic matter content ($\rho=-0.62$ in spring season, $\rho=-0.67$ in autumn season).

Contaminants of air and soil reduce the number and vitality of the soil fauna that decompose organic substances and provides its circulation in an ecosystem [11]. One of the effects of reduced microbial activity and slow decomposition of the plant residues is manifested by an increased depth of organic layer due to the accumulation of non-decomposed organic matter (Figure 3-5).

Figure 3. Soil profile on flotation tailing site FT 1

Figure 4. Soil profile on mine waste piles site MWP 3

Figure 5. Soil profile on mine waste piles site MWP 4

Research on the impact of gaseous pollutants and aerosols from the copper mine and metallurgical plant in Bor on the surrounding soil microorganisms [5] revealed that their effect is negative, and it increases with the proximity of the pollution sources. Thus, the number and diversity within the different groups of microorganisms in the soil decreased from locust stands outside of the pollution zone to the locations that are closer to the mining and smelting facilities.

The relatively small total content of soil microbes found in this investigation is a consequence of the direct and indirect effects of present pollution: the oxidation of the sulfur dioxide and the precipitation of atmospheric particulate matter of heavy metals on the surface of investigated mine soils, and contamination of the plant tissues which becomes a source of energy for the microorganisms after the decay.

CONCLUSION

The content of microorganisms in mine soils of black locust stands on copper mine wastes in Bor generally shows similar trends in spring and autumn season. Total micobial content prevails over the other groups of microorganisms, but their relatively small content reveals the negative effect of the pollution at the mine waste sites. While small number or absence of actinomyces results from a low humus content, increased number of ammonifiers on all investigated fields during the spring season results from fresh organic matter input.

Based on the the ratio of the number of different of soil microorganisms at the investigated sites following conclusions can be made: a) major part of the organic matter decomposes to the end-products, b) synthesis of humus out of the inter-products of organic matter decomposition is slow, c) synthesis of of fulvic acids occures, but their nature is not aggressive, d) further decomposition of the synthesized humic substances to the end products is either very slow, or was not identified. However, the overall picture of soil microflora on Bor mine soils clearly shows that the transformation process of organic matter under the black locust stands has been eastablished, wich significantly contributes to the development and ecological stability of revegetated sites.

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REFERENCES

1. Juma N. (1998): The pedosphere and its dynamic: a system approach to soil science, Edmonton, Canada, quality color press Inc, 1:315.
2. Kuzyakov, Y., Xingliang Xu, X. (2013): Competition between roots and microorganisms for nitrogen: mechanisms and ecological relevance, New Phytologist, 198: 656–669.

3. Markowicz , A., Woźniak, G., Borymski, S., Piotrowska-Seget, Z., Chmura , D. (2015): Links in the functional diversity between soil microorganisms and plant communities during natural succession in coal mine spoil heaps, Ecological research, 30 (6), pp 1005–1014.
4. Milijić, Z. (1997): Jalovišta rudnika bakra, njihov uticaj na životnu sredinu i metode rekultivacije, zbornik radova, V naučni skup 'Naša ekološka istina', 8-12. jun, Sokobanja.
5. Resulić, N. (1997): Heterotrofna mikroflora peskova na odlagalištima površinskih kopova EPS, Magistarski rad, Poljoprivredni fakultet, Beograd.
6. Resulić, N., Milićić B., Kuzmanović, Đ., Tomić, M. (2004): Uticaj štetnih gasova i aerosola iz rudnika bakra i metalurških postrojenja u Boru na mikrofloru okolnih zemljišta, Eko - konferencija 2004 , Tematski zbornik II, Ekološki pokret grada Novog Sada.
7. Schnüre, J.,.Clarholm. M., Rosswall, T. (1985): Microbial biomass and activity in an agricultural soil with different organic matter contents, Soil Biology and Biochemistry, Volume 17 (5), pp 611-618.
8. Six, J., Bossuyt, H., Degryze, S., Denef, K. (2004): A history of research on the link between (micro)aggregates, soil biota, and soil organic matter dynamics, Soil and Tillage Research, V79, (1), pp 7–31.
9. Wildman, H. (2014): Improving mine rehabilitation success through microbial management, Oil, Gas and Mining, 1 (2), pp 1-15.
10. Williams, S., Vickers, J., Goodfellow, M. (1984): New microbes from old habitats? In: Kelly, D.P., & Carr, N.G. (eds) The microbe 1984, II: prokaryotes and eukaryotes. Cambridge University Press, Cambridge, pp 219–256.
11. Wyszkowska, J., Kucharski, J.,Borowik,A., Boros, E. (2008): Response of bacnteria to soil contamination with heavy metals, Journal of elementology, 13(3), pp 443-453.

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SUPERCRITICAL FLUIDS - APPLICATIONS AND ECOLOGICAL IMPORTANCE

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ABSTRACT

The application of supercritical fluids as an alternative to conventional precipitation and extraction processes has been an active field of research and innovation during the past decades. The most important in many supercritical fluid applications is solvent power, that is, the ability to dissolve other substances. The most used supercritical solvent is carbon dioxide, somethimes modified by co-solvents such as ethanol or methanol. Most extraction applications are focused on natural products for human consumption, where the green status of carbon dioxide represents a clear benefit. Supercritical water is also used as supercritical fluid. Supercritical water received considerable attention especially as a reaction medium for reforming wastes and byproducts, being attractive from an environmental point of view. Perhaps the best-known application is supercritical water oxidation, which may lead to the total oxidation of organic waste. Supercritical fluid based processes actually offer new opportunities to meet the challenge of producing high purity, chemically and physically stable micro- or nano-particles with low solvent residues. Processes involving supercritical fluids require less energy and are environmentally friendly compared to traditional processes involving organic solvents. Supercritical fluids are cheap, inert and nontoxic.

Key words: Supercritical fluids, carbon dioxide, supercritical water, solvent.

INTRODUCTION

Supercritical fluids (SCF) are defined as any substance at a temperature and pressure above its thermodynamic critical point and which has a density close to or higher than its critical density [1]. Supercritical fluids possess properties of both gases and liquids, what makes them very attractive for material processing. The diffusivity in SCF is higher than the one in liquids, but viscosity is lower, facilitating mass transport. Because of the high compressibility, density and dissolving power can be tuned sensitively through small changes in pressure. Because of their tunable properties, supercritical fluids can be used in various applications with different nature of compounds [2, 3]. However, the critical point of most compounds is found at extremely high pressure (Pc) and/or temperature (Tc) conditions, as shown in table 1.

Supercritical fluids are often referred as existing in a state somewhat between gases and liquids. In fact they are gases at pressure and temperatures above those of the vapour-liquid critical point. [4] The really unique property of supercritical fluids is their ability to respond to small changes in pressure or temperature with large variations of density, without undergoing a phase change. Density is directly related to many other physical and chemical properties of a fluid. With small relative changes in pressure (or temperature), a supercritical fluid can be brought from relatively low density, where it can hardly dissolve anything, to liquid-like densities, where the molecules of the fluid can cluster around the molecules of solid or liquid solutes and bring them into the gas phase [5]. The use of the supercritical fluid eliminates or reduces the use of toxic or contaminant organic solvents and the elimination of the supercritical fluid from the final product can be easily accomplished by a simple depressurization. Most applications of supercritical fluids are developed around a higher pressure compartment or vessel and a lower pressure one. In the first, the supercritical solvent promotes dissolution/extraction/reaction or any other intended higher density-dependent effect. In the second one, decompression often leads to separation of products from the fluid [6].

Table 1. Critical properties of diverse solvents

Solvent	T_c (°C)	P_c (bar)
CO_2	31.1	73.8
Ethane	32.2	48.8
Ethylene	9.3	50.4
Cyclohexane	280.3	40.7
Toluene	318.6	41.1
Benzene	289.0	48.9
Water	374.2	220.5

Supercritical water and carbon dioxide are often used supercritical fluids. In the case of water, its properties as a solvent vary considerably as temperature increases, due to the gradual disruption of its three-dimension hydrogen bond network, which starts to occur well below the critical temperature (374 ºC). At high temperatures, water behaves as a highly polar "non-aqueous" solvent, dissolving hydrocarbons and precipitating ionic salts. It is also a highly reactive medium, promoting a variety of chemical reactions, as exemplified by the importance of hot, pressurised aqueous solutions (the so-called hydrothermal fluids) in geochemical processes. Supercritical water in these conditions is a highly reactive substance, and it can act as solvent, reactant and/or catalyst. Hydrolysis, oxidation and pyrolysis of organic compounds have probably been the most studied reactions.

As any other supercritical fluid, supercritical water has properties that can be fine-tuned by temperature or pressure.Temperatures and pressures may be chosen so that only partial oxidation of organic molecules will occur. The change of the dielectric constant of water with density can also be used to favor the formation of either polar or non-polar oxidation products. Extraction with carbon dioxide has been the most important application of supercritical fluids. In the case of carbon dioxide (the most used supercritical solvent), the supercritical region can be achieved at moderate conditions of pressure and tempreature, avoiding the degradation of thermolabile substances and providing simultaneously an inert medium suitable for processing easily oxidable compounds [7]. The advantages of carbon dioxide as solvent in processes involving products for human consumption are well known: it is, in fact, classified as generally regarded as safe, it has low toxicity and it becomes supercritical just above ambient temperature, an important feature when dealing with heat-sensitive substances. It is cheaper than most organic solvents, and, like other supercritical fluids, it has advantageous gas-like transport properties, such as lower viscosity and higher diffusivity than liquid solvents. Carbon dioxide is a polar substance, because it possesses a permanent quadrupole – an asymmetry of charge distribution where negative charge is pulled towards the outer oxygen atoms, and the carbon atom becomes positive. The biggest interest for the last decade has been the applications of supercritical carbon dioxide, because it has a near ambient critical temperature (31°C), thus biological materials can be processed at temperatures around 35°C. However it dissolves mostly low molecular weight, non-polar compounds. It is a poor solvent for many other molecules, with some notable exceptions, like perfluorinated ones. This makes extractions and fractionations using carbon dioxide very selective processes, although they can only be used for the few substances that CO_2 can dissolve in reasonable amounts. Supercritical carbon dioxide extraction of natural products from solid plant matrices is currently an established, mature application, with over one hundred industrial facilities of various sizes. Although proposed as a "green" process for the replacement of volatile organic solvents, its implementation resulted in each case from definite technological advantages. A perfect example is given by a recently built industrial facility for the extraction of the substance trichloroanisol from cork powder with supercritical carbon dioxide. The unit is operating in Spain [8]. Supercritical CO_2 is becoming an important industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact. The relatively low temperature of the process and the stability of CO_2 also allows to most compounds to be extracted with little damage or denaturing. In addition, the solubility of extracted compounds in CO_2 varies with pressure, permitting selective extractions. Phase diagram for carbon dioxide is shown on figure 1.

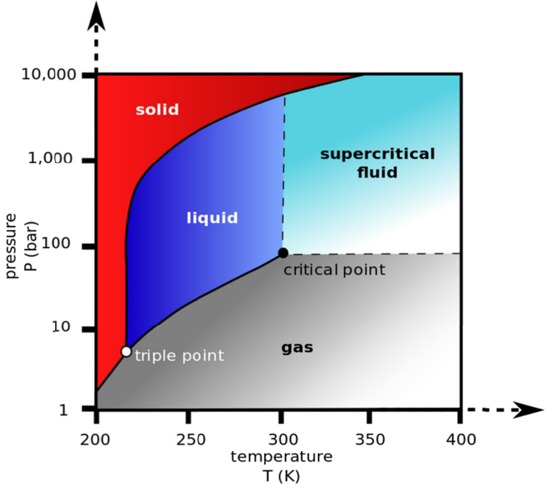

Figure 1. Carbon dioxide pressure – temperature phase diagram

In the case of CO_2, the fact that it is inert to oxidation and free radical chemistry makes it a desirable solvent for oxidation and free-radical polymerisation reactions. The discovery of DeSimone's group that addition of fluorinated tails to otherwise conventional homogeneous catalysts could increase their solubility in supercritical carbon dioxide greatly improved the possibilities of carrying out homogeneous catalysis in that solvent. Important application of carbon dioxide as reaction solvent that reached the commercial stage resulted from research collaboration between DuPont and the group of DeSimone in North Carolina [9].

GREEN CHEMISTRY IN SUPERCRITICAL FLUIDS

The principles of green chemistry and the principles of green engineering shortly afterwards have greatly increased the awareness of chemists and chemical engineers towards developing chemical processes that are safe and environmentally friendly [10]. Development of a green chemical process implies using the principles of green chemistry and engineering, from process inception in the research environment to process application on a commercial scale. Solvent substitution is one method that was promoted in the 1990 s for making chemical processes more environmentally friendly and reducing the amount of hazardous wastes. Aqueous solutions, supercritical fluids, ionic liquids, immobilized solvents, solventless conditions, low-toxicity organic solvents, and fluorous solvents, were identified as alternatives to using chlorinated, aromatic, volatile, and chlorofluorocarbon solvents [11]. Water and carbon dioxide, especially in their supercritical states, are primary candidates as solvents for green chemical processes, since they are compatible with the environment and have enhanced transport properties for reactions and separations [12].

SUPERCRITICAL FLUID PROCESSING

Among scientific fields investigated over the last 50 years, the use of supercritical fluids (SCF) was probably seen as one of the most promising and universally applicable techniques for a variety of applications: solvent free extraction and fractionation, particle design and engineering, chromatography, reactions, sterilization. These perspectives raised considerable academic and industrial efforts for bringing the supercritical fluid technology to maturity in each investigated field. By extension, the SCF acronym will herein be used for fluids operated either in supercritical conditions or in near-critical conditions, the fluid being in compressed liquid or dense gas state. In nuclear power generation with a supercritical water cooled reactor (SCWR), the use of supercritical water has a number of benefits compared with cycles that use pressurized water. Single phase heat transfer reduces system size since there is no boiling and the use of higher operating temperatures increases system thermodynamic efficiency up to 44%. Single-phase heat transfer improves system controllability since it is not necessary to control liquid in the reactor and this reduces the number of major components in the system. The SCWR is presently being developed by Canada, Europe and Asia as a Generation IV reactor concept. In the high temperature Generation-IV concepts, steam hydrolysis coupled with supercritical CO_2 power conversion provides a method to produce hydrogen at lower temperatures than when helium is used [13]. In refrigeration systems, CO_2 is seen as a replacement working fluid for hydrochlorofluorocarbons (HFC). CO_2 has about 8 times the volumetric capacity of conventional refrigerants and this increased energy density allows heat exchanger tubing diameters to be reduced by 30%, which makes the design of compact systems possible compared with conventional refrigerants. In heating and ventilating systems, CO_2 is seen as a competitive fluid for heat pumps.

In geological heat pipe systems, CO_2 is being considered as a working fluid. In a heat pipe system, heat from the Earth causes liquid CO_2 to be vaporized and transported. Fluid transport in the heat pipe system is by thermosyphon action, which eliminates the need for an electrical pump and use of CO_2 as the working-fluid eliminates the concern for groundwater contamination. In a system for producing hydrogen via hydrolysis, CO_2 is being proposed as the working fluid that is driven by solar energy. It can be concluded that many opportunities exist for using water or carbon dioxide as the working-fluids for clean energy devices. There is still much activity in the food, chemical and pharmaceutical fields in processing and product development with supercritical fluids. Supercritical fluids applied to food products have met with commercial acceptance as noted in the chemical engineering literature. Powderized solids and food composite plants from Natex (Germany), sesame, rice brand krill oil from UMAX (Korea), chlorogenic acid/ αlipoic acid diet supplement from coffee beans from UCC (Japan), saw palmetto + sesamin-E health foods from Suntory (Japan) and anti-hay fever nutraceuticals from Shiratori pharmaceuticals (Japan) are recent entries into the marketplace. In the manufacturing of fluoropolymer resins, there has been considerable commercial success in using supercritical carbon dioxide by DuPont (USA.) with proprietary licensed technology from The University of North Carolina at Chapel Hill. Fluoropolymers produced with supercritical carbon dioxide have enhanced properties fluoropolymers manufactured by conventional methods and the process generates very little waste compared with water-based methods. In polymer processing, supercritical carbon dioxide has been established as an efficient foaming agent for manufacturing thermoplastic parts with microcellular injection molding process as an example. The process allows production of high performance parts with high dimensional accuracy, up to 30% weight reductions, and low environmental impact compared with conventional methods. In pharmaceuticals and biomedical areas, however, although there are commercial developments that use supercritical fluids, industrial acceptance of supercritical fluid produced products including particle technology has lagged, which is probably due to the necessity of clinical studies that are required [14]. In the synthesis of inorganic materials, there are two reactive methods the thermal decomposition method and the supercritical hydrothermal synthesis method. The thermal decomposition method uses carbon dioxide whereas the supercritical hydrothermal synthesis method uses water. Either technique can use co-solvents or other additives depending on the products being synthesized. There are variations of the hydrothermal synthesis method that use organic solvents such as supercritical methanol, ethanol or mixed solvents. In thermal decomposition method, the metal complex precursor is dissolved in supercritical CO_2 and then decomposed with heat to form nanoparticles or films.

An interesting variation on these approaches is the reduction of a precursor that is dissolved into a polymer or surfactant in the presence of a CO_2–H_2 reducing atmosphere. Reduction of the precursor leads to the formation of highly dispersed organic–inorganic hybrid metal nanoparticles. New methods to form inorganic particles by reaction are being developed with probably one of the latest method being the reaction of particles in supercritical emulsions. The supercritical hydrothermal synthesis method proposed using water at high temperatures or supercritical conditions along with water-soluble precursors. Reaction of the precursors by mixing with water at high temperatures and pressures allows fine particles to form. This method has been used by many research groups to make a wide variety of materials. Much activity exists in using supercritical fluids in the areas of energy conversion, biomass gasification, biofuels, biodiesel, wet algae conversion and petroleum upgrading. Hydrothermal biomass gasification has the objective to generate hydrogen and methane with or without catalysts. Conceptually, water might be used as a solvent to reduce coke formation (solids) in the upgrading process, since it provides a source of hydrogen and is a diluent for coke precursors. In one basic study, water at densities of 100 to 200 kg m^{-3} lead to increased coke formation during reaction at supercritical conditions that was attributed to light components distributing in the supercritical phase and causing heavy components to concentrate in the heavy phase to form coke. Areas for environmental applications with supercritical fluid technology can be identified as waste treatment [15], biomass gasification, and polymer recycling Polymer recycling is being practiced on an industrial scale with supercritical methanol being used for chemical recycle of PET (polyethylene-terephthalate) bottles, subcritical water being used for chemical recycle of polyurethane, and subcritical water being used for chemical recycle of fiber reinforced plastics.

CONCLUSION

Supercritical carbon dioxide and water are extremely attractive solvents in a world where finding solutions for the problem of sustainability is becoming an ever more urgent matter. As a result of 30 years of intensive research, a host of applications has gone commercial, but many others are waiting to be adopted. Often the problems are not technical, but the fact that competing processes are easier and cheaper to apply, although totally unsustainable. Resistance to change will, as always, be hard to overcome, but it is expectable that many aspects of these proposed platforms will become a reality in the near future. Many chemical processes have been proposed that use supercritical carbon dioxide or supercritical water as the solvent. Presently, many commercial processes exist that use supercritical carbon dioxide, whereas those for supercritical water are limited in number and their application. Supercritical methanol and subcritical water are being applied on a practical scale for polymer recycle and this can be attributed to not only their favorable solvent properties but also to downstream separation and solvent recycle operations. As industrial equipment ages and new processes come online, supercritical water technology may become an industrial acceptable method for industrial producing. Systems for handling and processing biomass seem to depend on equipment materials of construction and solids handling. New system designs will be needed for conversion of biomass to energy or chemical products on a practical level. Industrial applications with new technology, however, are more likely to be applied if economic motivators exist. If economical advantages drive the adoption of neoteric solvents in industry, then environmental advantages can be expected as consequences, including reduced evaporative losses, reduced reliance on petrochemical-derived solvents, reduced hazardous waste and increased solvent recycling. SCF-based processes have great potential for processing of food or food-related products, pure pharmaceutical materials and drug-loaded composite particles. SCF extraction and fractionation processes are now established industrial techniques with several hundred plants in operation worldwide.

REFERENCES

1. Reverchon, E., Adami, R., Cardea, S., Porta, D., (2009), Supercritical fluids processing of polymers for pharmaceutical and medical applications, The Journal of Supercritical Fluids, 47(3), 484-492.
2. Cocero, M., Martín, J., Mattea, A., Varona, F., (2009), Encapsulation and co-precipitation processes with supercritical fluids: Fundamentals and applications, The Journal of Supercritical Fluids, 47(3), 546 - 555.
3. Weidner, E., (2009), High pressure micronization for food applications, The Journal of Supercritical Fluids, 47(3), 556-565.
4. Kikic, I. J. (2009), Polymer–supercritical fluid interactions, The Journal of Supercritical Fluids, 47, 458-465.
5. Kiran, E., (2009), Polymer miscibility, phase separation, morphological modifications and polymorphic transformations in dense fluids, J. Supercritical Fluids, 47, 466-483.
6. Sato, T., Mori, S., Watanabe, M., Sasaki, M., Itoh, N., (2010), Upgrading of bitumen with formic acid in supercritical water, Journal of Supercritical Fluids 55, 232–240.
7. Brunner, G., (2004), Supercritical Fluids as Solvents and Reaction Media, Elsevier Science, 47–52.
8. Beckman, E.J., (2004), Supercritical and near-critical CO_2 in green chemical synthesis and processing, J. Supercritical Fluids, 28 (2-3), 121-191
9. Brunner, G., (2009), Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes, J Supercritical Fluids, 47, Issue 3, 373-381
10. Anastas, P.T., Warner, J.C., (1998), Green Chemistry: Theory and Practice, Oxford University Press: New York, 30 - 33.
11. Anastas, P.T., (2002) Green chemistry as applied to solvents, Clean Solvents 819, 1–9.
12. Brennecke, J.F., Eckert, C.A., (1989), Phase equilibria for supercritical fluid process design, AIChE Journal 35, 1409–1427.
13. Yildiz, B., Kazimi, M.S., (2006), Efficiency of hydrogen production systems using alternative nuclear energy technologies, International Journal of Hydrogen Energy 31, 77–92.
14. Pasquali, I., Bettini, R. (2008), Are pharmaceutics really going supercritical? International Journal of Pharmaceutics 364, 176–187.
15. Serani, A.L., Aymonier, C., Cansell, F., (2010), Supercritical water for environmental technologies, Journal of Chemical Technology and Biotechnology 85, 583–589.

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ANALYSIS OF THE INDUSTRIAL RESULTS OF COPPER SLAG PROCESSING FROM THE RECONSTRUCTED COPPER SMELTER IN RTB BOR

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ABSTRACT

Copper slag, a by-product of pyrometallurgical production of copper, contains a significant amount of Cu, together with traces of other heavy metals.

Recovery of metals from the copper slags and utilisation of the copper slags are important not only for saving metal resources, but also for environmental protection. Flotation is an important technology for copper recovery from copper slag.

The project of New Copper Smelter in RTB Bor, besides the new flash smelting furnace (FSF) and the reconstruction of Pierce-Smith converter (PSC), includes more effective copper slag processing in the Bor flotation plant.

This paper presents an analysis of the results of the grinding circuits of the copper slag processing and discussion of its possible improvement.

Key words: copper, slag, smelter, grinding, hydrocyclone.

INTRODUCTION

The pyrometallurgical copper extraction from sulfide copper concentrates in the New Copper Smelter in RTB Bor will consist of concentrate drying, autogenous smelting in a flash smelting furnace (FSF) and matte converting process in a Pierce-Smith converter (PSC) [1, 2].

In order to increase process efficiency and reduce environmental impact, the New Copper Smelter in RTB Bor will include more efficient treatment of off-gas (its further processing in a sulfuric acid plant (SAP)) and processing of copper slag.

The Copper Mine Bor started copper slag processing from the reconstructed copper smelter in the Bor flotation plant (mill section B) in 2015, treating slag by flotation, after slow cooling, crushing and grinding [1-4].

The projected capacity of the copper slag processing is 340.000 tons per year with an average copper content of about 2 %. This amount of copper slag will be obtained from a flash smelting furnace (FSF) with copper content of 1,4 % and from Pierce-Smith converter (PSC) with copper content of 6 % [1, 2].

After the cooling process is obtained by copper slag with maximum grain size 150 mm, wherein an average copper content of 2 % and which can be further treated with flotation process [3-4].

After two stage of the grinding (projected feed size is 80 % -40 microns), the copper slag is conditioned with NaIPX 500 g/t and Dow-froth D250 12 g/t before being fed to the flotation process. The flotation rougher concentrate contains about 10 % of copper and than cleaning in the three stages of the flotation process to obtain projected quaility of the final concentrate. Projected yield of copper from the smelter slag is 84 %, a required quality concentrate based on copper content in the concentrate was 30 % [1].

Projected technological scheme of the smelting slag processing is shown in Figure 1 [1].

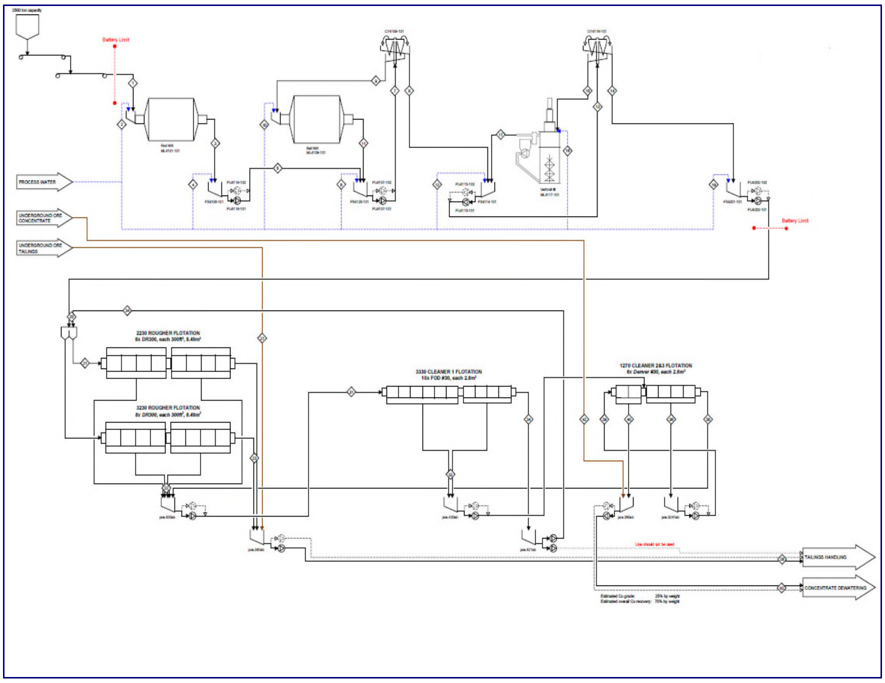

Figure 1. Projected technological scheme of the smelting slag processing in RTB Bor

Compared to the projected and reconstructed technological scheme, there have been certain changes in the copper slag process, as follows:

- grain size of the feed in the grinding process is GGK 6 mm,
- grinding process running in the two stage grinding with ball mill and vertical mill.

This paper presents an analysis of the results of the grinding circuits of the copper slag processing and discussion of its possible improvement.

EXPERIMENTAL PART

Grinding circuit of the copper slag processing is running in the two stages of grinding, in the ball and vertical mills. Grinding circuit also includes hydrocyclones in closed circuit to yield a product of the required size. Hydrocyclones are generally installed at an elevated position, above the grinding unit, so that the coarse underflow product can flow, by gravity, back to the grinding unit for further size reduction.

For a better control of the product size operation of hydrocyclones were analyzed. All products were sampled in equal time intervals and treated in laboratory. Results of grain size analyses and copper content by narrow size classes are given in Table 1 and 2 [5].

Table 1. Grain size analyses of ball mill - hydrocyclone products from copper slag processing

Size, (mm)	**Feed (F)**		**Overflow (O)**		**Underflow (U)**	
	Wt (%)	**Cu (%)**	**Wt (%)**	**Cu (%)**	**Wt (%)**	**Cu (%)**
+0.425	1.04	1.80	3.52	0.84	3.14	1.97
-0.425+0.300	3.00				4.32	
-0.300+0.250	2.51				5.10	
-0.250+0.150	16.11				23.40	
-0.150+0.075	30.96	1.98	21.68	1.07	35.19	2.42
-0.075+0.038	19.93	2.05	27.52	1.41	15.88	2.56
-0.038+0.020	8.54	1.82	14.43	1.49	4.73	1.96
-0.020+0.000	17.91	2.67	32.85	1.96	8.24	2.40
Total:	**100.00**	**2.06**	**100.00**	**1.51**	**100.00**	**2.41**

Table 2. Grain size analyses of vertical mill - hydrocyclone products from copper slag processing

Size, (mm)	**Feed (F)**		**Overflow (O)**		**Underflow (U)**	
	Wt (%)	**Cu (%)**	**Wt (%)**	**Cu (%)**	**Wt (%)**	**Cu (%)**
+0.425	0.46	2.36	0.27	0.35	0.55	2.19
-0.425+0.300	0.74				1.03	
-0.300+0.250	0.30				0.48	
-0.250+0.150	2.34				2.77	
-0.150+0.075	27.97	2.00	3.05	1.00	31.68	2.02
-0.075+0.038	38.68	2.22	28.14	1.07	43.59	2.54
-0.038+0.020	11.70	2.05	22.90	1.47	9.81	2.71
-0.020+0.000	17.81	2.43	45.64	2.00	10.09	2.38
Total:	**100.00**	**2.18**	**100.00**	**1.58**	**100.00**	**2.36**

Based on the results of the grain size analyses of the ball mill - hydrocyclone products in the first circuits of classification can be seen a large participation of a grain size class (-0.038+0) mm, up to 12.97 % with copper content 2.4 % in a hydrocyclone underflow which indicates on the classification inefficiency. This fact causes its additional overgrinding and an unnecessary increase in energy consumption.

Similar observations were observed during the analysis the results of the vertical mill - hydrocyclone products in the second circuit of classification. The particle size of the underflow is the controlling factor for determination of the efficiency of hydrocyclone. The distribution of a particular size (-0.038+0) mm in the feed between overflow (68.54 %) and underflow (19.90 %) indicate on inefficiency in a hydrocyclone classifier.

For efficient hydrocyclone operation it is necessary to operate as closed circuits, so that maximum coarse particles are removed. Also, since most hydrocyclone circuits operate in closed circuit, the recirculating load or ratio also needs to be determined.

RESULTS AND DISCUSSION

Based on the results of grain size analyses of the feed and the products of the classification as well as mass yield of the overflow γ_{OF}, the efficiency of the classification and the recirculating load is determined.

- **First classification:**

Recirculating load in a ball mill: $C = 154{,}52\%$
Mass yield of overflow: $\gamma_{OF} = 39{,}28$ %
Mass yield of underflow: $\gamma_{UF} = 60{,}72$ %
Efficiency of classification in a hydrocyclone: $E = 42{,}06$ %
Recovery of narrow size class in the overflow: $I_{-0.038} = 70{,}22$ %

- **Second classification:**

Recirculating load in a vertical mill: $C = 406{,}13$ %
Mass yield of overflow: $\gamma_M = 19{,}76$ %
Mass yield of underflow: $\gamma_p = 80{,}24$ %
Efficiency of classification in a hydrocyclone: $E = 37{,}07$ %
Recovery of narrow size class in the overflow: $I_{-0.038} = 45{,}89\%$

The efficiency of classification in the both hydrocyclones are 42.06 % and 37.07 %. A circulating loads are about 155 % in the first and about 406 % in the second circuit of the grinding-classification process. Obviously, the copper particles have a great probability to going with underflow.

The underflows are 60.72 % and 80.24 % of the total feed. These products of the hydrocyclone contains significant mass of the liberated copper particles, with average copper content about 2.4 %. Obviously, the particles of all size have a great probability of going with underflow. Inefficiency classifier is confirmed with insufficient yield of narrow size class (-0.038 + 0) mm in the first ($I_{-0.038}$ = 70.22 %) and second ($I_{-0.038}$ = 45.89 %) hydrocyclone.

Valorization of copper from hydrocyclone underflow by flash flotation cell may cause significant improvement in flotation process and as well as the whole process of copper slag processing.

Based on the obtained mass yield and copper recovery in the rough flotation of copper slag is carried out a mathematical prediction. Predicted data of technological parameters of copper flotation on the underflow of both hydrocyclones is given in table 3 [5].

Table 3. Predicted data of technological parameters of copper flotation on the underflows

Products	Mass yield, I_m (%)	Copper content, Cu [%]	Copper recovery, I_t (%)
Underflow I	16.65	4.39	32.39
Underflow II	9.70	10.87	44.71

Based on predicted mathematical data of the flotation results, from techno-economic point of view, obtained flotation results on the second hydrocyclone underflow (sand) are very satisfactory, taking into account the grain size and characteristics of the hydrocyclone underflow. Predicted mass yield, copper recovery and concentrate quality are 9.70 %, 44.71 % and 10.33 %, respectively. These facts give possibility for investigation an valorization of copper from hidrocyclone underflow by flash flotation cell.

Technological improvements in the existing industrial processing of copper slag with additional flotation on the second hydrocyclone underflow will enable a higher total copper recovery as well as decrease an energy consumption in the Bor flotation plant.

CONLUSION

Due to its complexity and heterogeneity, copper slag, in relation to the copper ore, is very different, both in terms of physical and chemical characteristics.

In an effort to solve future copper slag processing, these obvious differences cause different conceptions and optimization of technological schemes and technological parameters in Bor flotation plant.

By optimizing of the grinding and classification circuits and introduction of new technological solutions (flash flotation) and application of new flotation reagents, can be achieved significant improvement of the processing efficiency of copper slag in the flotation plant in Bor.

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REFERENCES

1. Environmental Impact Assessment Study, (2010). New Smelter and Sulphuric Acid Plant Project, Volume 1 – Main Project. University of Belgrade, Faculty of Metallurgy, SNC Lavalin.
2. Ivsic-Bajceta, D., Kamberovic, Z., Rogan, J., Cirkovic, M., Pavlovic, T. (2013). Analysis of copper losses throughout weak acid effluent flows generated during off-gas treatment in the new copper smelter RTB Bor. Metallurgical and Materials Engineering, 19 (3), 217-231.
3. M. Zikic, Z., Markovic, D., Andjelkovic, I., Stojadinovic, S., Sokolovic, J., Tanikic, D. (2015). Treatment slag from reconstructed smelter in Bor. Proceedings of the 7th Conference "The dumps of fly ash, slag and tailings in thermal power plants and mines", 22- 24 September 2015, Zrenjanin, Serbia, 233-240.
4. Sokolovic, J., Stanojlovic, R., Zikic, M. (2015) Sustainable processing of smelting slag in RTB Bor, Proceedings of III Scientific Conference with international participation "Politehnika 2015", December 4, 2015, Belgrade, Serbia, 233-238.
5. Guševac, M., (2016). Analysis of the results of industrial slag processing from new copper smelter RTB Bor, with the aim of improving the technology of the process, Diploma thesis, University of Belgrade, Technical faculty in Bor, Bor, Serbia.

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LEAVES OF TREES AS A LOW COST MATERIAL FOR DETECTION OF Cu AND Zn IN THE AIR

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ABSTRACT

A potential of using the needles/leaves of pine, linden and elder for detection of the environmental pollution, with the emphasis on air pollution with Cu and Zn was assessed. In the conditions of increased pollution, elder leaves had the highest Cu and Zn contents. Pine, linden and elder leaves indicated the environments with increased Cu levels, while linden leaves were better in the case of Zn. The detection of the Cu and Zn presence in the atmospheric deposition could be achieved by using the difference between element concentrations in washed and unwashed needles/leaves of all the three examined species, and especially of elder.

Key words: air pollution, copper, zinc, pine, linden, elder.

INTRODUCTION

Aboveground plant parts represent physical barrier for polluting substances during their transport through the air, providing surface for deposition and immobilization of solid particles and gasses. According to that, plants were identified with biological filters [1]. Foliar parts of both deciduous and evergreen trees fit into the general definition for passive samplers of the pollution in the environment. Passive sampling is based on the free flow of analyte molecules from the sampled medium (e.g. air) to a collecting medium (e.g. plant) as a result of the difference in chemical potential of the analyte between the two media [2]. Concentrations of polluting substances in/on the leaves are usually in good correlation with the concentrations in atmospheric deposition [3]. Because of that, the ability of plants to accumulate polluting substances from the air can be utilized for biomonitoring. Concentrations of deposited particles of different diameters, as well as metals, from the air on the surfaces of leaves were usually obtained by analyzing plant material before and after washing. This kind of washing simulates rain effect on the adsorbed polluting substances on the leaves [4,5]. A particle size is, unlike the composition, more important for the behavior in the atmosphere. Particles of diameter <2 μm can enter the stoma cavities [6]. Copper and zinc are essential elements for the activity of physiologically important enzymes that function as catalysts in the plants. Also, those elements may be released in some regions in excessive amounts [7]. Copper and zinc were found in the air as constituents of particles of diameter <1.1 μm [8] and <0.3 μm, in the surroundings of facilities for smelting and processing of copper ore [9]. Well known extreme air pollution in the town of Bor [10] and the surroundings represents a good base for assessment of the possibility of using pine current year needles, linden and elder leaves for the detection of Cu and Zn in the air as constituents of atmospheric deposition. Although continuous monitoring of air pollution in the studied area is being conducted, the data about imission of these elements are poor or missing.

MATERIAL AND METHODS

Sampling of current year needles and leaves was conducted during 2013, before a new smelter and a sulphuric acid plant started working. Plant samples were collected from 8 sampling sites within 6 zones. The urban–industrial (UI) zone represented a part of the town of Bor, nearest to the copper smelter (0.5–2.5 km), and along the area where the pollution was transported from the smelter by the prevailing wind (WNW). Dust from the tailing ponds, emissions from the thermal power and heating plants and traffic, were additional sources of pollution. The urban zone (U) in the town of Bor (>2.5 km SW of the copper smelter) was only periodically influenced by pollution episodes. The suburban zone (SU) represented the surroundings of the settlement, situated 2.5 km NW of the copper smelter, affected by pollution from the smelter and dust from the overburden dumps. The industrial zone consisted of the I1 and I2 sampling sites. The sampling site I1 belonged to the surroundings of the copper mine Veliki Krivelj (5.5 km N of the copper smelter), while the sampling site I2 represented the surroundings of the copper mine Cerovo (11 km NW of the copper smelter). Dust from the tailing ponds and open pits were the main sources of pollution in the industrial zone. The sampling sites R1 and R2 were a part of the rural zone: 1) R1-the surroundings of the village 4.5 km SE of the copper smelter, polluted with dust from the flotation tailing ponds of the copper mine Veliki Krivelj; 2) R2-the surroundings of the village 6.5 km SE of the copper smelter, under the pollution from the smelter. The control (C) zone represented the surroundings of the village Gornjane (17 km N of the copper smelter) without the impact of the pollution from the mining and metallurgical facilities. The samples of leaves and current year needles were collected at 1.5 to 2 m height above the ground from outer branches of the canopy. The foliar samples were divided into two halves in a laboratory. One half was retained as an unwashed sample (UL), while the second half was thoroughly washed (WL) with running distilled water for about 1 min at room temperature, to remove the particle fraction deposited on the surfaces of leaves/needles. After air drying at room temperature, plant samples were ground to a fine powder and stored at room temperature until analysis. The samples of leaves and needles were digested in a microwave oven [11]. Concentrations (μg/g dry weight) of Cu and Zn in extracts were determined by ICP-AES, in the Mining and Metallurgy Institute Bor (Serbia). The element concentrations in unwashed and washed needles/leaves sampled in the zones under the influence of copper production facilities were compared by paired

Wilcoxon Signed-Rank test. The values of Enrichment factor (EF) were calculated by dividing the concentration of a certain element in the needles/leaves from a polluted zone by the concentration of the same element in the needles/leaves from the control zone. The values of EF>2 indicate environmental pollution.

RESULTS AND DISCUSSION

Copper. Pine needles (UL, WL) from almost all the sampling sites had lower Cu content than the linden and elder leaves, except WL from the UI zone (Figure 1a,b). Higher Cu concentrations in the elder leaves (UL, WL) compared to the linden leaves were determined in the samples from the UI and SU zone (the sites nearest to the copper smelter), as well as in the samples from the R2 site (in the prevailing wind direction). The Cu contents in the linden and elder leaves from the other sites were similar. These data suggested that in the conditions of the increased environmental pollution, elder leaves absorbed higher contents of Cu than leaves of pine and linden. As opposed to that, linden and elder leaves had naturally approximate Cu contents, at the sites which were not directly affected by the emission from the smelter. The highest concentrations of Cu in the leaves (UL, WL) of pine, linden and elder were detected in the samples from the UI, SU and R2 sampling sites, which was the consequence of the vicinity of the dominant pollution source and the influence of the prevailing wind direction. The values of EFs for Cu in the UL and WL of the examined plant species were >2 at all the sampling sites, indicating that Cu was present in higher concentrations in the samples from the town of Bor and the surroundings than in the unpolluted environment (C zone) (Figure 1c,d). Very high values of the EFs were calculated for the UL and WL of pine, linden and elder from the UI and R2 sampling sites. According to the obtained results, pine, linden and elder leaves could indicate the environments with the increased Cu levels. However, it cannot be defined which plant species was more efficient for that purpose. From the copper smelter and the flotation tailing ponds in Bor, higher contents of the polluting substances with the high share of Cu were emitted, than from the overburden dumps and mining activities in the Veliki Krivelj and Cerovo copper mines (sites I1 and I2).

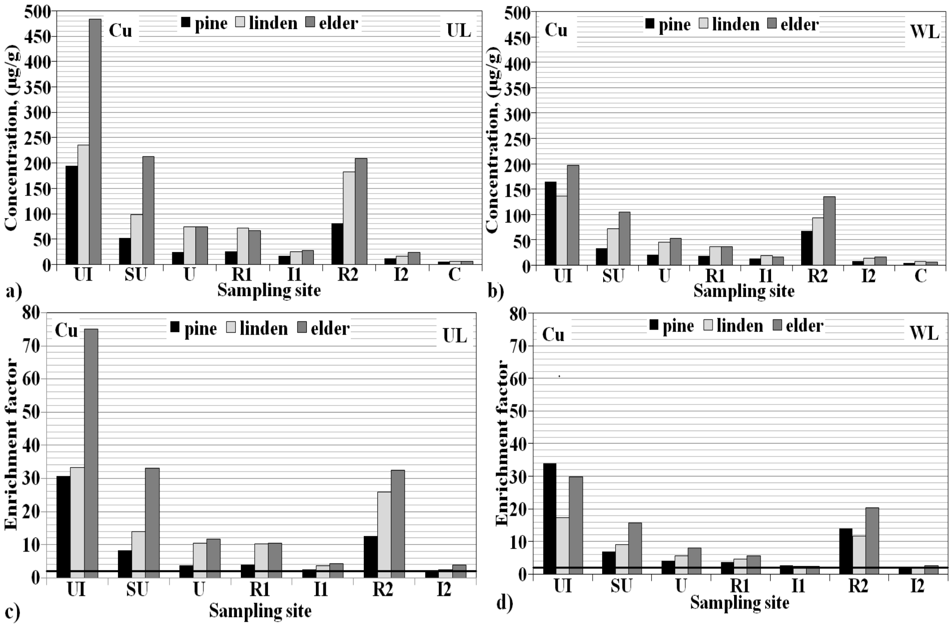

Figure 1. Copper in the leaves of pine, linden and elder: a) concentration in the UL, b) concentration in the WL, c) Enrichment factor for the UL, d) Enrichment factor for the WL. Black horizontal line EF=2.

Statistically significant decrease of Cu concentrations for all the three examined plant species was achieved by washing the leaves with water (Table 1), suggesting that pine, linden and elder needles/leaves could be used for determination of Cu presence in the atmospheric deposition. The lowest differences in the concentrations between UL and WL were calculated for the pine needles (except at the I2), compared with the results for linden and elder. The highest differences in the concentrations were observed for the samples from the UI zone, where elder had the highest ability of retaining the Cu on the surfaces of the leaves. Al-Alawi and Mandiwana [12], as well as Sun et al. [13], determined several times lower concentration differences between unwashed and washed pine needles than the ones obtained in our study. The contents of Cu in the WL of linden and pine were higher than the defined critical for the leaves and needles of higher plants (20 µg/g) [14,15], at all the sampling sites, except for the industrial and control zone. This value was exceeded in the pine needles from the UI, SU, U and R2 sites. Considering that pine, linden and elder have developed some strategies by which they adapted to high Cu concentrations in the environment.

Table 1. Differences (μg/g) between Cu contents in the UL and WL of pine, linden and elder

Sampling site	pine[a]	linden[a]	elder[a]
UI	31.60	98.57	287.20
SU	19.32	26.75	109.31
U	5.03	29.76	22.29
R1	8.28	36.24	30.83
I1	4.04	7.62	11.24
R2	13.69	90.22	74.84
I2	4.41	3.83	7.97

[a] Statistically significant difference according to the Wilcoxon Signed–Ranks Test ($p<0.05$)

Zinc. The unwashed and washed linden leaves compared to the foliar parts of pine and elder had lower Zn content at the majority of the sampling sites, except the UL from the R1 and R2 (Figure 2a,b). Elder leaves (UL, WL) compared to pine needles and linden leaves mainly contained more Zn. In the unpolluted zone (C), UL and WL of elder also had the highest Zn content, which suggested that elder leaves contained naturally higher Zn concentrations, compared to the pine and linden leaves.

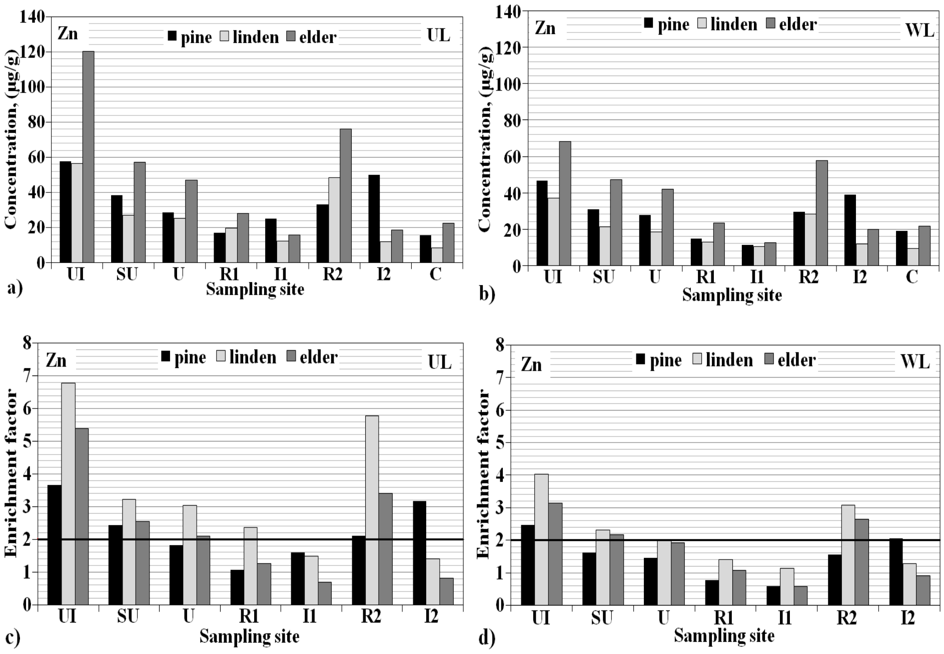

Figure 2. Zinc in the leaves of pine, linden and elder: a) concentration in the UL, b) concentration in the WL, c) Enrichment factor for the UL, d) Enrichment factor for the WL. Black horizontal line EF=2.

The values of EFs for Zn in the UL for at least one plant species from almost all the sampling sites (except I1) indicated the increased Zn content (Figure 2c,d). Unlike that, EFs for WL indicated the enrichment with Zn only at the sampling sites UI, SU and R2. EFs>2 for UL were observed at more sampling sites in comparison with EFs for WL, which suggested the influence of Zn from the atmospheric deposition on the enrichment with Zn. The highest values of EFs for leaves (UL, WL) of pine, linden and elder, were for the samples from the UI zone, where the copper smelter and flotation tailing ponds are located. Linden leaves were better for the use in defining the polluted environments, due to the higher EFs compared to the other two examined species. A decrease of Zn concentrations after washing with water was statistically significant for all the three analyzed plant species (Table 2). The highest Zn quantities were washed off the linden and elder leaves from the UI and R2 sites. For the sites nearest the copper smelter in the UI and SU zones, the highest difference in the Zn concentrations was for the elder leaves. According to such results, the leaves of the examined plants, and especially of elder, could be used for determining the presence of Zn in the atmospheric deposition. The concentration difference of Zn between unwashed and washed pine needles from the industrial zone in the study by Al-Alawi et al. [12] was up to 10 times higher compared to the results from the UI zone of Bor. The concentrations of Zn in the WL of pine, linden and elder were mainly not higher than excessive (>50–100 μg/g) [15], except in the elder leaves (>50 μg/g) from the sites UI and R2. Similarly as for Cu, it was concluded that elder probably has adaptation abilities developed for the increased Zn concentrations in the leaves.

Table 2. Differences (μg/g) between Zn contents in the UW and WL of pine, linden and elder

Sampling site	**pine**[a]	**linden**[a]	**elder**[a]
UI	11.02	19.52	52.24
SU	7.77	5.64	10.17
U	1.13	6.91	5.19
R1	2.24	6.80	5.00
I1	13.96	1.94	3.28
R2	3.66	20.07	18.48
I2	10.95	0.07	-1.24

[a] Statistically significant difference according to the Wilcoxon Signed–Ranks Test ($p<0.05$)

CONCLUSION

In the conditions of the increased environmental pollution, elder leaves had higher Cu contents than the leaves of pine and linden. Linden and elder leaves probably have naturally approximate Cu concentrations at the sites which were not affected by the emission from the copper smelter. According to EFs, pine, linden and elder leaves could indicate the increased Cu levels in the environments. Higher contents of the polluting substances with the high share of Cu were emitted from the copper smelter and the flotation tailing ponds in Bor than from the overburden dumps and mining activities in the Veliki Krivelj and Cerovo copper mines. Pine, linden and elder leaves could be used for determination of Cu presence in the atmospheric deposition. The elder leaves (UL, WL), compared to pine needles and linden leaves contained more Zn at almost all the sampling sites. Elder leaves probably have naturally higher Zn concentrations, compared to the pine and linden leaves. Zn from the atmospheric deposition has influenced the enrichment with Zn. Linden leaves are better for the use in defining the polluted environments with Zn, due to the higher EFs, compared to the other two species. The leaves of the examined plants, and especially elder, could be used for determining the presence of Zn in the atmospheric deposition. It seems that pine, linden and elder have developed some strategies by which they adapted to high Cu concentrations in the environment, which also could be said for the elder in the case of Zn.

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REFERENCES

1. Przybysz A., Sæbø A., Hanslin H.M., Gawroński S.W., (2014) Accumulation of particulate matter and trace elements on vegetation as affected by pollution level, rainfall and the passage of time. Sci Total Environ, 481, 360–369.
2. Górecki T., Namieśnik J., (2002) Passive sampling. Trend Anal Chem, 21(4), 276–291.
3. Aničić M., Spasić T., Tomašević M., Rajšić S., Tasić M., (2011) Trace elements accumulation and temporal trends in leaves of urban deciduous trees (*Aesculus hippocastanum* and *Tilia* spp.), Ecol Indic, 11, 824–830.
4. Kocić K., Spasić T., Aničić Urošević M., Tomašević M., (2014) Trees as natural barriers against heavy metal pollution and their role in the protection of cultural heritage, J Cult Herit, 15, 227–233.
5. Ataabadi M., Hoodaji M., Najafi P., (2012) Assessment of washing procedure for determination some of airborne metal concentrations, Afr J Biotechnol, 11(19), 4391–4395.
6. Song Y., Maher B. A., Li F., Wang X., Sun X., Zhang H., (2015) Particulate matter deposited on leaf of five evergreen species in Beijing, China: Source identification and size distribution. Atmos Environ, 105, 53–60.
7. Kabata-Pendias A., Mukherjee A.B., (2007) Trace elements from soil to human, Springer-Verlag Berlin.
8. Pan Y., Tian S., Li X., Sun Y., Li Y., Wentworth G. R., Wang Y., (2015) Trace elements in particulate matter from metropolitan regions of Northern China: Sources, concentrations and size distributions. Sci Total Environ, 537, 9–22.

9. Csavina J., Landázuri A., Wonaschütz A., Rine K., Rheinheimer P., Barbaris B., Conant W., Sáez A.E., Betterton E.A., (2011) Metal and metalloid contaminants in atmospheric aerosols from mining operations. Water Air Soil Pollut, 221, 145–157.
10. Serbula S.M., Milosavljevic J.S., Radojevic A.A., Kalinovic J.V., Kalinovic T.S., (2017) Extreme air pollution with contaminants originating from the mining-metallurgical processes. The Sci Total Environ 586:1066−1075.
11. U.S. EPA, "Method 3050B: Acid Digestion of Sediments, Sludges, and Soils," Revision 2. Washington, 1996, p.12.
12. Al-Alawi M.M., Mandiwana K.L., (2007) The use of Aleppo pine needles as a bio-monitor of heavy metals in the atmosphere. J Hazard Mater, 148, 43–46.
13. Sun F., Wen D., Kuang Y., Li J., Li J., Zuo W., (2010) Concentrations of heavy metals and polycyclic aromatic hydrocarbons in needles of masson pine (*Pinus massoniana* L.) growing nearby different industrial sources. J. Environ. Sci., 22, 1006–1013.
14. Pählsson, A.-M.B., (1989) Toxicity of heavy metals (Zn, Cu, Cd, Pb) to vascular plants. Water Air Soil Pollut., 47, 287–319.
15. Radmacher P., (2003) Atmospheric heavy metals and forest ecosystems. Federal research centre for forestry and forest products. Hamburg.

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TOXICITY OF ESTIMATION METHODS FOR RESIDUAL STRESSES AND STRESS CORROSION RESISTANCE IN BRASS PRODUCTS

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ABSTRACT

Residual stress in metallic materials, due to effects of stress corrosion, may cause occurrence of cracks or even complete destruction of the material. In order to estimate the level of residual stress in coldly processed ammunition cartridge cases made of brass, according to standard EN ISO 196, we use test method with the mercury(I)-nitrate and ammonia copper-sulphate. However, working with mercury and solvents contaminated with mercury is toxic, so due to environmental protection and working conditions of employees, method with mercury(I)-nitrate becomes problematic.

The method based on the sensitivities to stress corrosion of amonia seems to be more environment-friendly.

This papper presents an overview of the results of residual stress and toxicity of applying method with mercury (I)-nitratne and ammonia copper-sulphate.

Key words: residual stresses, mercury(I)-nitratna methods, ammonia copper-sulphate methods.

INTRODUCTION

The residual voltage is the voltage inside the components that is present after all external acting forces have been removed. It appears by pressing or by tightening of materials [1]. For many cases, particularly in the the throat bushings, stresses are so large it has to be applied high temperature annealing for it's removal[2].

Some liquid metals are the cause why tense copper alloys fracture, leads to embrittlement. In the first place it is an elementary mercury and its compounds. The melted connective tissue, melten tin and the melted sodium can also cause breakage at the copper alloys [2].

Fracture due to stress corrosion of copper alloys might be caused by effect of many types of aqueous solutions of such as the sulphates, nitrates, nitrites, chlorides but nonetheless aqueous solution of ammonia is the major contributor in the environment that causes the stress corrosion. Ammonia stress corrosion is considered to be the main hazard for copper alloys, therefore the estimate that the ammonia is efficient medium for detection of cracks sensitive copper alloys is justified [3].

As well in all other systems, with the mutual influence of the corrosive matter and voltage, it comes to activation of the process of stress corrosion, especially in the case of alpha brass in ammonia environment, where smudges remain on the surface. Copper content in the alloy reacts with ammonia forming a complex ion which reacts with the hydroxyl ions producing a copper oxide [3]. Copper oxide grows to metal from which it originated and prevents further reaction unless there has been an independent process.

Based on the previous studies, the methods based on ammonia have been identified as the most prospective to cause a stress corrosion fracture at brass. But compared to mercury solutions, cracks will not be as large (ASTM B 858) [4,5]. Nevertheless, compounds that have ties to ammonia will also cause an breakage of toned brass: evaporative of methylamine, dimethylamine, trimethylamine, aniline and triethanolamine will do fracture because of stress corrosion after somewhat a longer exposure.

Mattsson invented solution for testing toned brass, consisting of ammonia and copper sulphate which is alkalized to pH 7.2 with ammonium hydroxide [5,6]. According to NATO EPVAT methods it has been predicted two methods for determining residual stress at ammunition: a solution of mercury (I)-nitrate and methods a solution of ammoniacal copper(II)-sulphate [7,8].

EXPERIMENTAL

Comparative tests were carried out by applying method of mercury nitrate and ammoniacal copper sulphate methods, and on the ammunition of 5.56 mm made of brass with designation CuZn28, i.e. CuZn30. In order to obtain comparative results, in particular in the area of the throat bushings, bushings are not calcine. The investigations were performed according to the document AC/225 EPVAT NATO standards.

a) Mercury-nitrate methods

The acidic solution of mercury (I) nitrate is a quick method that is used to detect high and even moderate stress in many copper alloys. Samples shall be at first defatted, and then dissolved in a 40% solution of nitric acid to remove the oxides, and then washed under running water and immersed for 30 minutes in an aqueous solution of 10g of mercury nitrate, $Hg_2(NO_3)_2$ with 10 ml of concentrated nitric acid per liter. After the specified time the samples were removed from solution, washed with cold water and wiped of the excess mercury from the surface.

The samples are immediately visually inspected and for more precised checing is used magnifying glass. Detected cracks are brought into the test protocol. Some international standards (ASTM) prescribes that performing of evaporation of amalgamated mercury on a hot plate after deleting samples. Control of strangeness of mercury is carried out by measuring the masses of the sample, which can be then visually and microscopically controlled by the presence of stress corrosion cracks [9,10].

b) Ammoniacal copper - sulphate methods

The ammoniacal copper sulphate is a complex compound of the full name tetraamine copper (II) sulphate-hydrate, Cu $(NH_3)_4SO_4xH_2O$. It arises due to reaction ammonia on the copper (II)- sulphate pentahydrate which is a complex compound in which four of water molecules are related to the central copper ion, while the fifth water molecule of watter is related to sulfated ion $Cu(H_2O)_4SO_4$ xH_2O. In water it provides a characteristically light blue coloration. If this solution works with ammonia, it will come to reaction where the ammonia molecules replace water molecules related to the copper ion, and it will arise deep blue (indigo) solution of tetraamine copper sulfate hydrate.

The samples, as well as in the method with mercury nitrate are first defatted and than deluged in a 40% solution of nitric acid over a period of 30 second. Then they are well rinsed with liquid and distilled water and immersed in the ammoniacal copper sulphate solution. A solution of ammoniacal copper sulphate is prepared in the next way: 12.6 g of copper sulphate pentahydrate is dissolved in about 500 ml of distilled water (light blue solution) and then it we add 75 ml of ammonia of density 0.91 g/ml (25% ammonium-hydroxide, NH_4OH). The colour of solution exceeds into dark blue, and the measuring bottle shall fill to 1000ml.

The samples are dipped in the solution and leaving in it 8 hours ± 30 minutes. The solution must be freshly prepared for testing and can be used only once. The temperature of the solution at the beginning of the test must be 21 ± 3 ° C. The samples are then removed from solution, rinsed under running, distilled water and then dried. For the detection of stress corrosion crack, we examine with magnification glass or a microscope with enlargement 10 to 15 x. We observe the whole surface of the of samples, especially places with effective technical requirements.

RESULTS

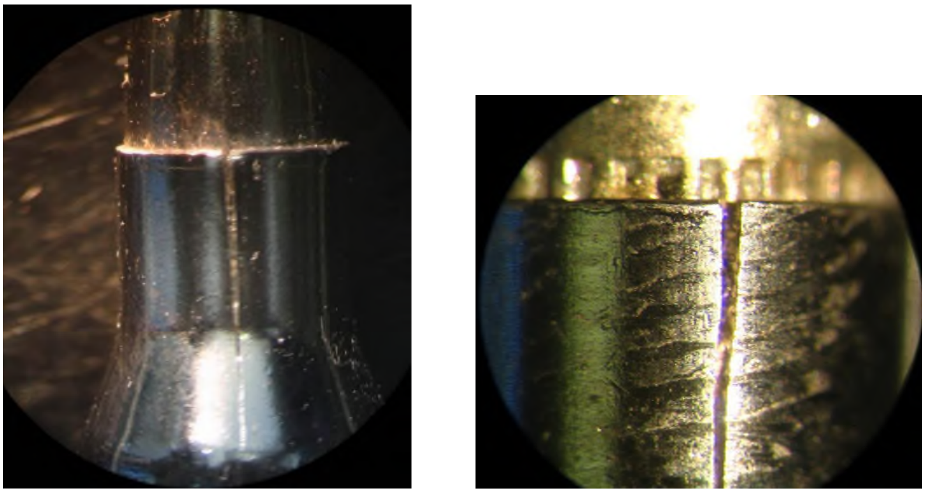
The macroscopic appearance of one part of the treated cartridge cases from both groups are shown in Figure 1. From the figure is clearly seen that the outer surface of cartridge cases differs. For a better insight, for each group of treated cartridge case samples, test results are displayed separately.

Figure 1. Treated samples with methods with mercury-nitrate solution (right) and ammoniacal copper-sulphate a solution (left)

a) Test results mercury-nitrate methods

After treating the cartridge cases with naked eye it has been observed bursting on the mouth of the cartridge cases. Of the 10 tested cartridge cases, 10 was cracked. Cartridge case is cracked even longitudinal. The bullet was viewed under the microscope with a magnification of 16 and 40 times (figure 2). Immediately after removal of cartridge case from a solution it is observed migration of a substance (probably mercury) on the cartridge cases. Crack is clearly visible.

After a few days the same samples were again observed under a microscope. Migration of the matter were gone and cracks were partially filled with the silver-coloured substance , (this looks like a complete cartridge cases which is coated with a layer of mercury). It can be concluded that mercury is substance that is moving after the experiment. After letting off samples for a few days, mercury with basic metal formed amalgam and fills the crack that now looks like it's welded. Amalgam is initially plastic, but later it solidifies. If there are small cracks, layer of mercury covers cracks and they are not noticed.



a) b)

Figure 2. Treated samples methods with mercury-nitrate a)16 x b) 40 x

b) Test results of ammoniacal copper-sulphate methods

In contrast to the the preceding, in this group of treated samples, cracks are not visible to the naked eye, but under a microscope with a magnification 16 i 40 times, cracks are identified, figure 3.4. (of the 15 tested cartridge cases 15 pieces is cracked). Most of cracks are longitudinal, but there are has even horizontal (this makes network of cracks), figure 4.c,

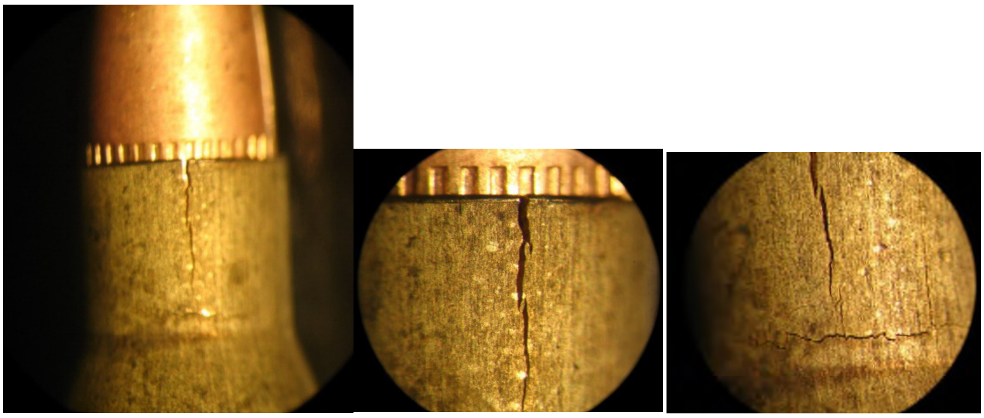

a) b) c)

Figure 3. Treated samples ammoniacal copper-sulphate a solution of

DISCUSSION

When the method with mercury-nitrate is aplied, naked eye can be registered spraying of cartridge case, while with the method with ammonia copper-sulphate, it can not, but it must be viewed under magnification of at least 10-15 times.

Methods with mercury-nitrate is incomparably faster for testing, ammunition in the solution is treated for 15 minutes, instead ammunition in a solution of ammoniacal copper sulphate 8 hours. If they are needed rapid test results method with mercury-nitrate has the advantage. Testing with modified ammonia vapors gave shorter time spraying of samples (about 30 minutes).

From the aspect of toxicity, according to the classification of materials that are used for both methods, mercury-nitrate is the most toxic substance and it is classified in the group of highly toxic substances. Ammunition tested with mercury-nitrate represents a major problem for its further treatment. In this study, metal mercury covers the entire surface of the bushing, so bushing should be deposited in the metal barrels which should then be buried in the ground at a designated place, it should not be incinerated as the used ammunition in open space. Incineration these ammunition would lead to evaporation of metallic mercury and its dissipation into the surrounding space, this may cause poisoning of workers with mercury vapors. Anyway, incineration also brings also to environmental pollution and working environment.

For these reasons, method with ammonia copper sulphate has the advantage in applying, but disadvantage of this method is the unpleasant smell of ammonia and its corrosive effect. With the necessary compliance of measure of protection (work in a ventilated area - digester, personal protection), poisoning ammonium- hydroxide and copper -sulphate is reduced to a minimum. A special advantage of this method over mercury nitrate method is a procedure with munitions tested and can be completely the same as with the 'Skart' ammunition, i.e. can be done burning the ammunition that will not cause no additional of pollution in the relation to burning 'Skart' ammunition[11].

From the aspect of impact on the environment having in view of the toxicity of substances which are applied for testing method, method with ammonia copper sulphate is more favorable. Its advantage is particularly evident in the process treated with ammunition. Metal mercury covers the entire surface of the cartridge cases, it migrates in the environment or in the ammunition if ammunition is disposed in the open in the form of vapor and metal mercury. When we are working with the ammonia copper-sulphate, ammunition burning does not bring any additional pollution.

Method with solutions for testing should be also regulated, so that the solutions does not discharge into the sewage flow which leads directly to the aqueous flows until we finish treatment with them. In doing so, it is much easier to carry out the treatment of ammoniacal copper- sulphate than a solution of mercury-nitrate, because for the treatment of mercury nitrate solution metallic mercury allocates which must be disposed under special measures.

Insight into the prices of chemicals that is used in these two methods shows that the method with ammonium copper-sulphate is cheaper method than the mercury-nitrate 2 to 5 times depending on the manufacturer. The raw materials for method with ammonia copper sulphate are domestic products and easier to obtain.

In our country, for testing residual stress we apply method with mercury-nitrate solution which is prescribed by standards EN ISO 196.

CONCLUSION

Based on the above, it can be drawn the following conclusions:

- On samples that are not annealed comes to 100% spraying cartridge cases when we apply any method with mercury-nitrate solution or with solution of ammoniacal copper-sulphate.
- Both methods can be successfully used for the determination of residual stresses and for distinguishing of samples that have not or that have went through the annealing treatment.
- From the point of toxicity for workers, impact on the environment and economy, method with ammonia copper-sulphate has the advantage and it is justified its introduction as a method for testing residual stress and inclination to stress corrosion fracture.
- Advantage of the method with mercury nitrate is the speed of its implementation and notofication of cracks with the naked eye.

REFERENCES

1. Proto Manufacturing Ltd.: X – Ray Diffraction Residual Stress Measurement, 2011.: www.protoxrd.com/assets/rsintro.pdf
2. Allan Jones J.: Stress Relief, Annealing and Hardnes, Firearm Examiner Training: http://projects.nfstc.org/firearms/module05/fir_m05_t06_06.htm

3. B. F. Brown: Stress Corrosion Cracking Control Plan 3. copper Alloys, NTIC U.S. Department of Commerce, 1975.: www.dtic.mil/dtic/tr/fulltext/u2/a012872.pdf
4. ASTM B 858: Standard Test Method for Determination of Susceptibility to Stress Corrosion Cracking in Copper Alloys Using an Ammonia Vapor Test, 1995.
5. Deborah J. Owen: An Assesment of Test Environment for the Stress Corrosion Cracking of small Caliber Brass Cartridge Cases, NTIC U.S. Depatment of Commerce, 1974.: www.dtic.mil/dtic/tr/fulltext/u2/780011.pdf
6. ASTM G37: Standard Practice for Use of Mattsson's Solution of pH 7.2 to Evaluate the Stress- Corrosion Cracking Susceptibility of Copper-Zinc Alloys ,1998 (2011).
7. NATO EPVAT Testing: AC/225 (Com. III/SC.1) D/200, Army Armaments Group (NAAG).
8. ASTM B 154: Standard Test Method for Mercurous Nitrate Test for Copper and Copper Alloys, 1995.
9. SRPS EN ISO 196: Plastično prerađeni bakar i legure bakra - Otkrivanje zaostalog napona - Ispitivanje živa(I) nitratom, ISS, Beograd, 2011.
10. SnO 8279: Ispitivanje prisustva zaostalih napona u čauri pomoću živa-nitrata, Odeljenje za SIM, TOC, Beograd, 1997.
11. Mahmoud Wazne, Santhi Sri Billapati, Christos Christodoulatos, Kristin L. Jasinkiewicz, Kimberly E. Hogrelius, Michael Hespos, Christopher Haines: Environmentally friendly Replacement Test for the Mercurous Nitrate Test for Copper and Copper Allyos: www. rcosmos.gr/srcosmos/showpub.aspx?aa=8492

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DETERMINATION OF THERMAL SHOCK RESISTANCE OF GLASS FRIT USING NONDESTRUCTIVE TEST METHODS

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ABSTRACT

In this study, the behavior of glass-ceramics synthesized from a glass frit FFW (Final Flotation Waste) originated from the RTB Bor Company, was investigated. Thermal shock resistance was monitored, in order to assess the possibility of application of such waste material. Thermal shock of the samples was conducted using water quench test. Ultrasonic measurements were used as a nondestructive quantification of thermal shock damage in the bulk of the specimens. Phase composition was determined by X-ray powder diffraction analysis. Results of the thermal shock stability testing indicated that level of destruction of sample is about 43% for 20 cycles of water quench test.

Key words: Final Flotation Waste (FFW), Glass-ceramic, Thermal shock, Ultrasonic velocity.

INTRODUCTION

Extraction of copper, particularly flotation enrichment and pyrometallurgical processing, results in formation of waste materials which produce major environmental pollution problems. Final flotation waste dumps and discarded slag from smelting furnace occupied large areas of land and causes permanent pollution of soil, water and air. Utilization of such waste materials, that is predominantly of silicate composition (consisting of fayalite, magnetite and glass), is very significant, not only heaving in mind the reduction of significant amounts of industrial waste, but also applying such waste as a potential raw material for the launch of a new technology initiatives [1-2]. Recycling the industrial waste material is a very frequent subject of numerous works [2-8], in which a glass-ceramics is being obtained by the process of vitrification.

The known thermal shock resistance is the most important characteristic for determining the material properties when concerning their implementation. The thermal shock resistance is measured in terms of the number of cycles that material under test can withstand subjected to sudden temperature changes [9-16].

The goal of this paper was to present thermal shock characteristics of glass-ceramics synthesized from a glass frit of FFW in order to determine the possibilities of their usage.

EXPERIMENTAL

Materials

Tab. 1 show chemical composition of the FFW determined by using the X-ray fluorescent analysis (PANalytical AXIOS XRF Spectrometer). The FFW was sampled at the end of flotation process, prior to deposition on the landfill.

Table 1 The chemical composition of FFW [2]

Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	K_2O (%)	MgO (%)	ZnO (%)	SO_2 (%)	CuO (%)	TiO_2 (%)	Na_2O (%)	Mn_3O_4 (%)	P_2O_5 (%)
52.10	34.27	4.89	4.58	1.22	0.79	0.79	0.50	0.49	0.36	0.31	0.07	0.07

The phase's ratio of FFW was determined by the Powder Cell (PCW) program using the structural models of fayalite [17], magnetite [18], and hematite [19]. The obtained results of XRPD analysis showed that FFW is composed of fayalite (75.00 %) and magnetite (25.00 %) (Fig. 1.), with some glass which cannot be detected by using the X-ray diffraction analysis.

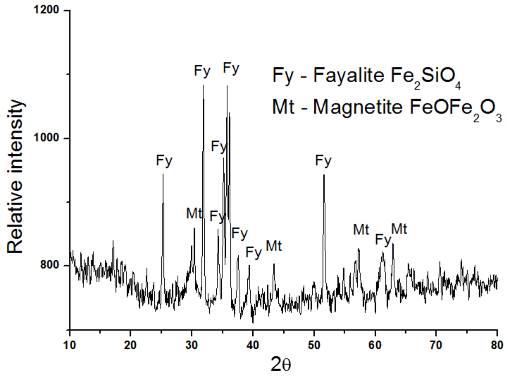
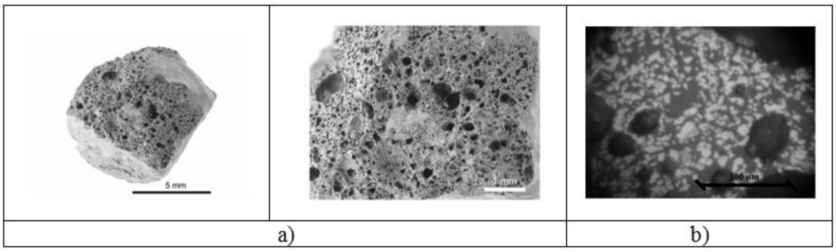


Figure 1. X-ray powder diffraction diagram of FFW [2]

In order to obtain a frit, FFW sample was heat-treated at 1300 °C, within 2 - 4 h, followed by rapid cooling in water. Obtained frit was pulverized in a vibrating mill, and then sample molded in a cylindrical mold (diameter 1 cm and height 1 cm) was sintered in duration of 4 hours at a temperature of 1100 °C. Resulting glass-ceramics possess bubbling structure (where the caverns around 0.02 to 0.03 mm, rarely about 1mm) (Fig. 2a.), which is a consequence of the emanation of gasses due to heat treatment. Such structure has good thermo-insulated properties.



a) b)

Figure 2. a) – Macro photography and b) microstructure of the glass-ceramic samples obtained by frit sintering at 1100 °C [2]

Glass-ceramic samples consists of the glassy phase and anhedral rarely subhedral crystals (Fig. 2b.), in which two phases were observed: lighter - hematite, and darker - magnetite phase. This is a solid solution of hematite - magnetite. Magnetite crystals cannot be specifically identified because they appear as a separate phase in the hematite crystals, and their boundary elements cannot see, because they have not developed the appropriate form.

XRPD pattern of the glass-ceramic sample is shown in Fig. 3. We could conclude that magnetite from FFW arises by strong oxidation of hematite, and fayalite in the amorphous glass [2, 3, 20, 21].

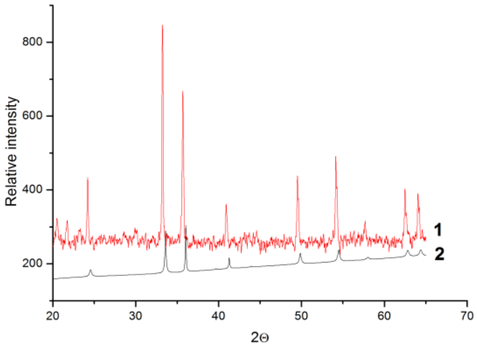
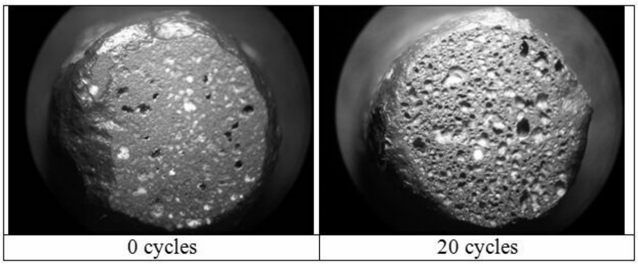


Figure 3. X-ray powder diffraction diagram of glass-ceramic obtained by frit sintering at 1100 °C (1), theoretical diagram of hematite (2) [19]

Water Quench Test

Thermal shock behavior of the samples was investigated using water quench test experimental method (ICS 81.080 SRPS B.D8.308 former JUS B. D8. 306). Samples were cylinders with same length and diameter (1 cm). Each thermal shock cycle is consisted of several consequent steps of rapid cooling into water [16, 22-26]. First, the samples were dried at 110 °C for 24 h; then put into an electrical furnace at 950 °C and hold in it for 15 minutes. Then, the samples are cooled in water for 3 minutes and dried before return into the furnace at 950 °C. This procedure is repeated until the appearance of first cracks (fracture). The number of cycles before the appearance of cracks (fracture) is taken as a measure of material thermal resistance. The standard fracture is defined as complete destruction of a sample, or destruction of 50% or more percentages of surface, coherent prior to this testing. Fig. 4 is shows the sample surfaces before and after the certain number of cycles.



0 cycles | 20 cycles

Figure 4. Samples before and during water quench test [2]

For the determination of destruction level of samples, image analysis was applied using Image Pro Plus Program. Samples were photographed before and during test, in order to measure the level of destruction. Destruction level of the samples is given as function of a number of cycles of water quench test (Fig. 5).

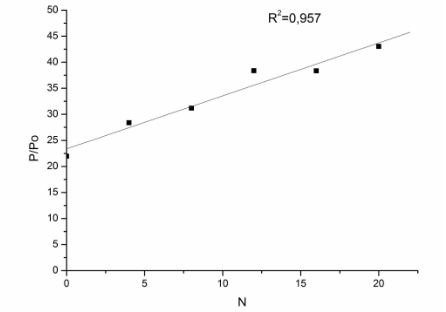


Figure 5. Destruction level of the samples (P/Po) versus number of cycles N. P represents damaged surface area and Po is non-damaged surface area (surface before testing) [2]

Ultrasonic determination of dynamic Young modulus of elasticity

Various publications have dealt with the practical application of Ultrasonic Pulse Velocity Testing (UPVT) to characterize and monitor the properties of industrial refractory materials non-destructively. The UPVT method has been considered in detail in ref. [16, 27-29]. Briefly, pulses of longitudinal elastic stress waves are generated by an electro-acoustical transducer that is held in direct contact with the surface of the sample under test. After travelling through the material, the pulses are received and converted into electrical energy by a second transducer.

The velocity and dynamic modulus of elasticity are calculated based on equations (1) and (2) well documented in the references [16, 27-29].

$$V = \frac{L}{T} \text{ (m/s)} \tag{1}$$

where L is the path length (m) and T is the transit time (s).

$$E_{dyn} = V^2 \cdot \rho \cdot \left(\frac{\left(1+\mu_{dyn}\right) \cdot \left(1-2\mu_{dyn}\right)}{1-\mu_{dyn}} \right) \tag{2}$$

where V is the pulse velocity (m/s), ρ is the bulk density (kg/m^3) and μ_{dyn} is the dynamic Poisson ratio.

The measurement of ultrasonic velocity was performed using the equipment OYO, model 5210, according to the standard testing procedure (SRPS D. B8. 121. former JUS. D. B8. 121.). Young's modulus of the samples was calculated using ultrasonic velocities obtained by UVPT [27-30].

Changes in ultrasonic velocity and Young modulus of elasticity are given in the Figs. 67.

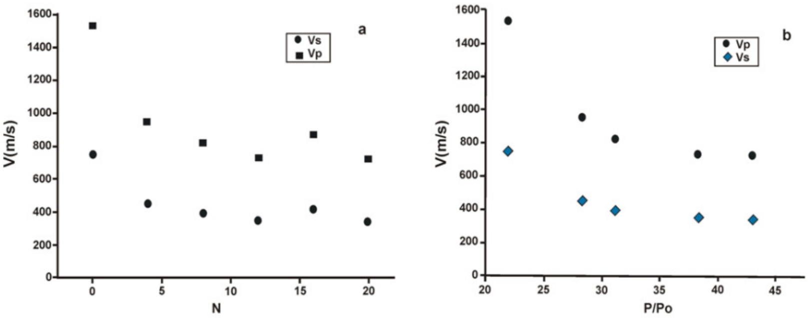


Fig. 6. *Changes of ultrasonic velocity versus: a) number of quench cycles (N), and b) level of degradation*

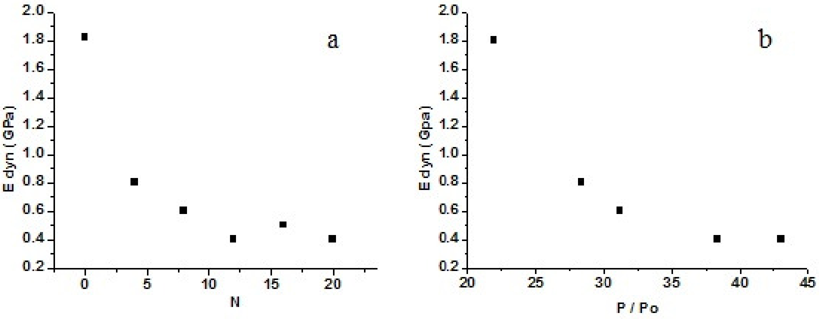


Figure 7. Changes of Young modulus of elasticity versus: a) number of quench cycles (N), and b) level of degradation

Strength Degradation

The ultrasonic velocity change suggest that materials were very stable during testing, as decrease of the velocity was not very different comparing with the velocity through the sample before the water quench test. These results indicate also that the number of nucleated cracks and crack propagation did not resolute in the rapid degradation of strength and Young modulus of elasticity, thus, samples showed an excellent thermal shock behavior.

Knowing the compressive strength of the material before exposure to the thermal shock testing, and ultrasonic velocity before and after testing, the compressive strength values were calculated from the equation 3 [16, 22-24, 30]:

$$\sigma = \sigma_0 \cdot \left(\frac{V_{P,S}}{V_{P0,S0}} \right)^n \qquad (3)$$

where σ_o is a compressive strength of the material before the exposure to the thermal shock testing (σ_o was determined experimentally), $V_{P,S}$ is the velocity of ultrasonic waves (longitudinal and transversal) after testing, $V_{P0,S0}$ is the velocity of ultrasonic waves (longitudinal and transversal) before testing, and n is material constant ($n = 0.488$). This equation was used for the calculation of both the longitudinal and transversal ultrasonic velocity.

The results for strength degradation obtained by ultrasonic measurements and calculated using the equation 3 were presented in the Figs. 8a and 8b respectively.

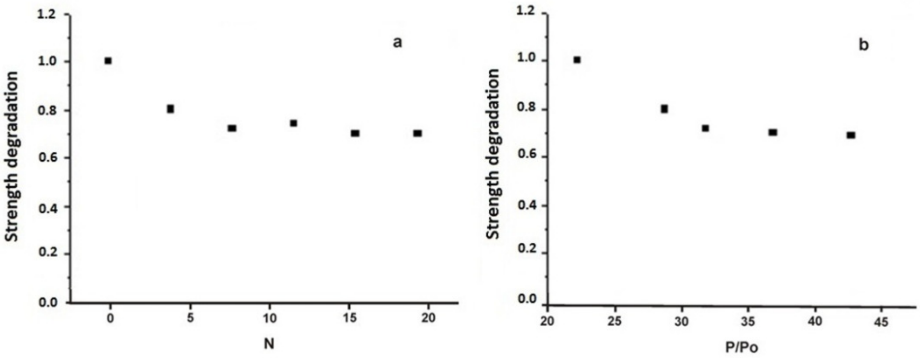


Figure 8. Strength degradation versus: a) number of quench cycles (N), b) level of degradation

DISCUSSION

The level of destruction, defined as P/Po ratio (where P is damaged surface and Po is non-damaged surface eg. surface before quenching) increases with a number of quench experiments (N). It is a very important to note that certain level of destruction was observed in the samples even before the quenching (22%). This level of destruction will affect thermal shock behavior of the samples, thus a higher level of destruction will lead to a lower thermal stability.

The samples were experimentally investigated till 20 cycles of thermal shock test. The obtained level of destruction after 20 cycles of thermal shock test was 43 %. Such thermal shock level pointed out good thermal stability of the samples.

Ultrasonic measurements pointed out that significant change in ultrasonic velocity, as well for Young modulus of elasticity were observed after 4 cycles. After only 4 cycles of thermal shock test ultrasonic velocity decrease to 38 % (from 1530 to 970 m/s) of velocity before the quenching. Similar results were obtained for the Young modulus of elasticity. After 4 cycles, Young modulus of elasticity decreased for 57 %, from 1.8 to 0.8 GPa. During testing, the changes were not such rapid, at the end of experiment, ultrasonic velocity (Vp) was 720 m/s which was one half the value measured before testing. After 20 cycles, modulus of elasticity decreased for 76 %, from 1.8 to 0.4 GPa.

Strength degradation during testing did not show such behavior, since after 4 cycles was calculated to be 80 % of strength at the beginning of the experiment.

CONCLUSION

Glass ceramic samples were synthesized using glass frit of FFW as basic material. The thermal shock resistance was investigated using water quench test accompanied with the image analysis of the degradation during thermal shock testing and the ultrasonic pulse velocity measurements.

Obtained results pointed out that:

- Final flotation waste could be successfully used for synthesis of the glass ceramic material.
- Obtained glass ceramic material showed good thermal shock resistance properties. After 20 cycles of water quench tests the level of destruction was about 43 %.
- Results of the thermal shock stability testing suggested that glass ceramic samples could be used in the applications with rapid temperature changes.

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REFERENCES

1. Davenport W., King M., Schlesingr M., Biswas A.K., Extractive metallurgy of copper, Chapter 4, Pergamon, USA 2002
2. Cocic M., Application of the flotation waste from the RTB Bor for glass – ceramics. PhD thesis, Faculty of Mining – Geology, University of Belgrade, Belgrade, 2012

3. Gorai B., Jana R. K., Premchand, Characteristics and utilisation of copper slag, Resources, Conservation and Recycling 39, 299–313, 2003
4. Coruh S., Nuri Ergun O. and Cheng T., Treatment of copper industry waste and production of sintered glass–ceramic, Waste Management & Research, 24, 234-241, 2006
5. Romero M. and Rincon, J. Ma, Preparation and properties of high iron oxide content glasses obtained from industrial wastes, J. Eur. Ceram. Soc., 18, 153–160, 1998
6. Scarinci G., Brusatin G., Barbieri L., Corradi A., Lancellotti I., Colombo P., Hreglich S. and Dalligna R., Vitrification of industrial and natural wastes with production of glass fibres, J. Eur. Ceram. Soc., 20, 2485–2490. 2000
7. Karamanov A., Taglieri G., Pelino M., 'Iron-rich sintered glass–ceramics from industrial wastes', J. Am. Ceram. Soc. 82, 3012–3016, 1999
8. Karamanov A., Aloisi M. and Pelino M., Vitrification of copper flotation waste, J. Hazard. Mater., 140, 333–339, 2007
9. Hasselman D. P. H., Elastic Energy at Fracture and Surface Energy as Design Criteria for Thermal Shock, J. Am.Ceram. Soc., Vol 46, No 11, 535-540, 1963
10. Nakayama J., Direct Measurments of Fracture Energies of Brittle Heterogenius Materials, J.Am.Ceram.Soc., Vol 48., No 11., 583–587, 1965
11. Nakayama J., Ishizuka M., Experimental Evidence for Thermal Shock Damage Resistance, Amer.Cer.Soc.Bull., Vol. 45 , No.7, 666-669, 1965
12. Kingery W. D., Factors Affecting Thermal Stress Resistance of Ceramic Materials, J.Am.Ceram.Soc., Vol 38, No 1, 3-15, 1955
13. D.P.H. Hasselman, Theory of Thermal Shock Resistance of Semitransparent Ceramics Under Radiation Heating, J. Am. Ceram. Soc., 49, 103-104, 1966
14. R.C. Bradt, Fracture Measurements of Refractories: Past, Present and. Future, Am. Ceram. Soc.Bull., 67, 1176-1178, 1988
15. Posarac M., Dimitrijevic M., Volkov Husovic T., Devecerski A., Matovic B., Determination of thermal shock resistance of silicon carbide/cordiertite composite material using nondestructive test methods, Journal of the European Ceramic Society, 28, 1275-1277, 2008
16. Pošarac-Marković M., Majstorović J., Devecerski A., Matović B., Volkov – Husović T., Young's Modulus Evaluation and Thermal Shock Behavior of a Porous SiC/cordierite Composite Material, Sci. Sinter., 47, 289-297, 2015
17. Smyth J R., American Mineralogist, Fayalite: AMMIA 60, 1092-1097, 1975
18. Fleet M E, Magnetite, Acta Crystallogr. B, 37, 917-920, 1981
19. Maslen E. N., Streltsov. V.A., Streltsova N.R., Ishizawa N., Hematite, Acta Crystallogr. B, 50, 435-441, 1994
20. O'Neill H. St. C., Systems Fe-O and Cu-O: thermodynamic data for the equilibria Fe-"FeO", Fe-Fe_3O_4 "FeO"-Fe3O4, Fe_3O_4-Fe_2O_3, Cu-Cu_2O, and Cu_2O-CuO from emf measurements., American Mineralogist, 73, 470-486, 1988
21. Mackwell S. J., Oxidation kinetics of fayalite (Fe2SiO4), Physics and Chemistry of Minerals, Phys Chem. Minerals., 19, 220, 1992

22. Volkov Husovic T.D., Thermal Stability Testing of Refractory Specimen, Journal of Testing and Evaluation, Vol 35, No 1, 1-5, 2006
23. Boccaccini, D.N., Romagnoli, M., Veronesi, P., Cannio, M., Leonelli, C., Pellacani, G., Husovic, T.V., Boccaccini, A.R. Quality Control and Thermal Shock Damage Characterization of High-Temperature Ceramics by Ultrasonic Pulse Velocity Testing, International Journal of Applied Ceramic Technology, 4, (3), 260-268, 2007
24. S. Martinovic, J. Majstorovic, V. Vidojkovic and T. Volkov-Husovic, Modeling of strength degradation during water Quench test of low cement high alumina castable, Ceram-Silikaty, 54, 169-175, 2010
25. S. Martinovic, J. Majstorovic, V. Vidojkovic and T. Volkov-Husovic, Influence of the Damage Level during Quenching on Thermal Shock Behavior of Low Cement Castable, Science of Sintering, 42, 211-219, 2010
26. S. Martinovic, Testing Influence of Sintering Temperature on Thermal Stability of Low Cement High Alumina Refractory Castable, doctor dissertation, TMF, Belgrade 2011
27. Fawzy A., Charles E. Semler, Prediction of Refractory Strength Using Non Destructive Sonic Measurements, Am. Ceram. Soc. Bull., 64 (12), 1555-1558, 1985
28. F. A. Berutti , A. K. Alves , and C. P. Bergmann, Relationship between the ultrasonic velocity and the degree of sintering of alumina-based materials, Mater. Des. 31, 3996–4000, 2010
29. S. K. Nyiogi, A. C. Das, Prediction of the Thermal Shock Behaviour of Castable Refractories by Sonic Measurments, Interceram, Vol 43, No 6, 453-457, 1994
30. T. D. Volkov Husovic, J. Majstorovic, M. Cvetkovic, Thermal Stability of Alumina Based Refractory, American Ceramic Society Bulletin, Vol 85, No 3, 14-15, 2006

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USAGE OF CATHODE RAY TUBE WASTE GLASS FOR THE PARTIAL SUBSTITUTION OF AGGREGATE IN CEMENT MORTAR

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ABSTRACT

Sustainable building is one of the key requirements in contemporary civil engineering aimed at reducing the harmful impact on the environment. Since the turn of twenty first century, it has been insisted on usage of recycled materials which could, at least in part, substitute traditional materials. Even though the TV sets with cathode ray tubes are no longer being produced, the amount of cathode ray tube glass (CRT) on the waste disposal sites have still been increasing. Regarding the specific chemical composition of the CRT glass, the recycling process is not simple. This paper presents the potential for usage of waste cathode ray tube glass as a partial substitution of aggregate in cement mortar.

Key words: environment, recycling, CRT glass, cement mortar.

INTRODUCTION

Electronic waste increases at a much higher rate than other solid wastes in the world. According to the assessment of the United Nations University, electronic waste will be increased and it will reach almost 50 million tons until 2018 [1]. For instance, out of 45.7 million tons of accumulated electronic waste in 2016, 6.3 million tons is the glass from TV sets and computer monitor screens. Although the production of TV sets with cathode tubes is discontinued, the amounts of cathode ray tube glass are still increasing. The production of c*athode* r*ay tube* glass increased, along with the rising demand of TV sets and Computer screens until the end of the previous century. However, scientific progress brought about new technologies of TV and computer screens manufacturing known as TFT (*Thin Film Transistor*) and LCD (*Liquid Crystal Displays*) which since the turn of 21st century entirely extinguished further production of cathode ray tubes. Table 1 presents the statistical data of Maria Socolof et al. [2] where one can see the number of globally produced screens. From the table one can clearly find out how much the new types of screens affected the reduction of the CRT screen production.

Table 1. Number of produced screens in the world, in millions of units [2]

Screen type	1998	2002	2010	2011	2012	2013	2014	2015	2016
CRT	80,7	83,3	36	21	18	12	7	5	5
LCD	1,3	32,2	178	197	205	222	238	250	261
Total:	82,0	115,5	214	218	223	234	245	255	266

CRT devices make up as much as 43% of electronic waste in the USA. It is estimated that there are around 232 million CRT devices still in use, so considerable amounts of these devices end up on the waste disposal sites each year, despite the fact that they almost cannot be found in the market. It is considered that around 85% of these devices will be collected in the following ten years. The existing recycling centers do not have sufficient capacity to stockpile and recycle the estimated quantities of CRT devices. There is a large problem occurring in the process of CRT glass recycling: it is almost twice as costly to recycle the cathode ray tubes as other electronic waste. In the USA the cost of transport and total recycling of 1 kg of glass costs among 0.14 and 0.24 dollar [3].

China is the world's largest producer, consumer and exporter of electronic equipment. At the same time, it faces big problems caused by accumulation of electronic waste, and illegal import of the waste from other countries *[4]*. In response to the considerable increase of electronic waste and potential deleterious effects on the environment, the Chinese government enacted a set of measures and laws regulating collection of the waste, its storing and its recycling process. It is estimated that the amount of waste CRT glass will be considerably increasing in China until the end of the current year.

A record number of 20 million units of CRT devices was sold in Europe in 1996. Since then, there was a gradual decline of selling, and ten years after this date, the selling was halved. Since 2011, the CRT devices have practically not been sold in Europe, but at the same time the amount of CRT waste on waste disposal sites started to increase *[5]*. Nowadays, it is not possible to find any CRT monitor or TV set in the electronic appliance shops. However, these devices survived in the households, and it is estimated that around 50-150 thousand tons of CRT screens end up annually on the waste disposal sites in Europe. The predictions of Fernando Andreola et al. is that the amount of collected CRT will not decline in the future period *[6]*.

CRT GLASS AS A PARTIAL REPLACEMENT OF FINE AGGREGATE IN CEMENT MORTARS

There are two types of cathode ray tubes: black-white and color cathode ray tubes. Three fundamental glass elements of CRT screen are *neck glass*, *funnel glass* and panel (*panel glass*). Their share in the total mass differs and it is: 1%, 33% and 66%, respectively. Neck glass, even though its mass share in the screen is small, contains around 25% of lead, which is far more than other parts. The funnel is the largest part of the cathode ray tube and it contains around 20% of lead. The panel is the front, visible part of the cathode ray tube and it almost contains no lead (0-3%).

Waste glass can be used for production of cement mortars in two ways. One possibility to use it as a filler, substituting a portion of natural aggregate. The other possibility is to use finely milled waste glass as a substitution for a part of cement when making the mortar. Further in the text will be presented the test results of the mortar where a part of aggregate was replaced either by panel glass or by funnel glass of CRT screens.

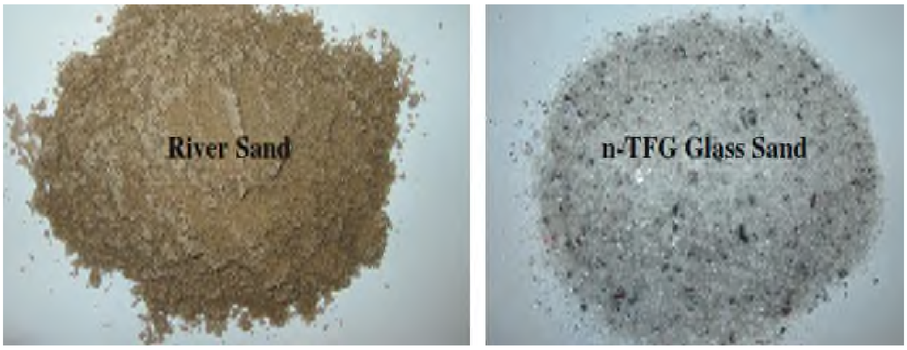

Figure 1. appearance of natural aggregate (left) and milled CRT glass (right)

Hui Zhao et al. [7] tested the properties of a mortar where a portion of natural river aggregate was replaced by CRT funnel glass. The funnel glass was not treated by nitrous acid to remove the present lead, but it was used in its original form. Fine river aggregate was replaced by CRT glass in the amount of 0%, 25%, 50% and 75% of its mass. On the same occasion, 25% of standard Portland cement was replaced by mineral admixtures – fly ash (4 mortar admixtures – FA series) and granulated slag (4 mortar admixtures GGBFS series), so a total of eight mortar mixtures were made. In figure 1 is displayed the appearance of natural aggregate (left) and recycled funnel glass, with particle fineness lower than 4 mm (right).

By testing the mortar consistency using Slump flow test, it was found that increasing the share of CRT aggregate in the mixture causes an increase of the spread diameter. Such trend can be explained by the fact that the grain of the glass aggregate has a smoother edge in comparison to the natural river aggregate, and that it "absorbs" incomparably less water than the river aggregate. The increase of the cathode glass replacement share (instead of sand) causes an increase of fresh mortar density in comparison to the control mixture without CRT (Figure 2) [7].

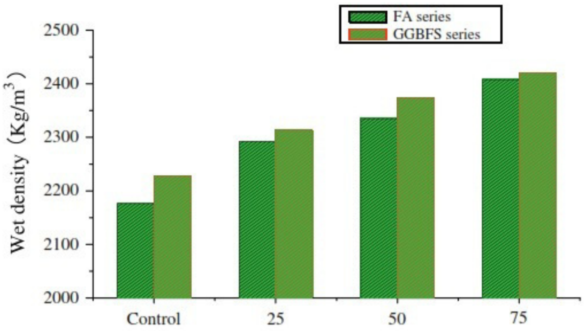

Figure 2. Density of fresh mortar depending on the replacement share of glass instead of aggregate *[7]*

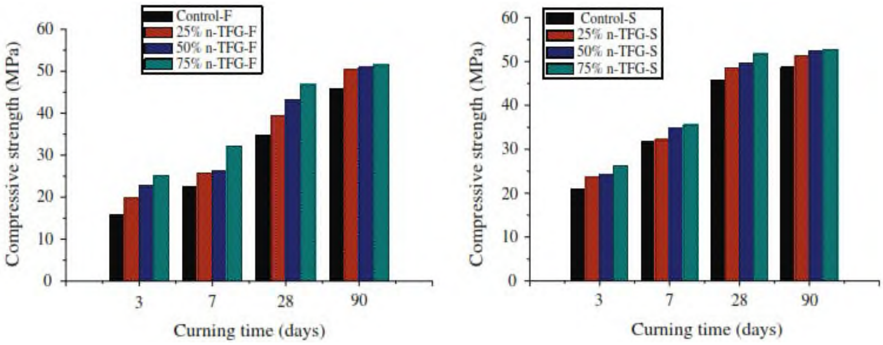

Figure 3. Effects of replacement of natural aggregate by CRT glass on the compressive strength of mortar at the age of 2, 7, 28 and 90 days *[7]*

Compressive strength was tested at the mortar age of 3, 7, 28 and 90 days. The test results bay Hui Zhao et al [7] are displayed in figure 3. It can be concluded that he mortars with the glass admixture had a higher compressive strength than the reference mortar at all the ages.

Hui Zhao et al. in the paper [8] researched the effects of replacement of complete natural aggregate by two types of CRT glass on the cement mortar properties. The first type was the CRT funnel glass which contained a certain amount of lead (*marked in the paper as MG*), while the other type of the glass underwent the lead separation treatment (*marked in the paper as G*). In this paper as well, 25% of the standard Portland cement was replaced by mineral admixtures – fly ash (*3 mortar mixtures*) and granulated slag (*3 mortar mixtures*). One of the conclusions is that on the occasion of replacement of the total river aggregate using the recycled glass, there occurs an increase of spread diameter on the test table [8]. In the table 2 are presented the results of compressive strengths of mortars with various aggregates and mineral admixtures at the age of 28 and 90 days. Firstly, it can be concluded that the batches of mortar with granulated slag have higher values of strengths and higher values of static modulus of elasticity in comparison to the batches of mortar with fly ash, with the same type of aggregate. Also, the mortar batches made with the CRT glass which contains lead have higher values of mechanical strengths in comparison with the batches of mortar made with two other types of aggregates, at the same age. .

Table 2. Compressive strength, flexural strength and static modulus of elasticity with various aggregates and mineral admixtures at the age of 28 and 90 days [8]

Mortar batch:	Compressive strength [MPa]		Flexural strength [MPa]		Static modulus of elasticity [GPa]	
	28 days	90 days	28 days	90 days	28 days	90 days
R-F	28,42	44,23	5,23	6,38	7,89	11,61
MG-F	40,21	49,25	5,63	6,72	12,47	13,75
G-F	38,75	47,29	5,56	6,68	10,26	13,64
R-S	29,04	42,92	5,46	6,10	8,23	10,48
MG-S	44,91	45,95	5,86	6,64	13,25	13,37
G-S	39,93	44,86	5,58	6,58	10,32	11,68

** R – river aggregate; F- fly ash; S – granulated slag*

In the Laboratory of building materials of the Faculty of Civil Engineering and Architecture of Niš the tests of the effects of replacement of natural aggregate by panel CRT glass on the properties of mortar in fresh and hardened states were also conducted. For making of the mortar, cement CRH CEM I 52,5R was used. For making of reference mortar, fine aggregate from the South Morava river from the screening plant „Vodogradnja" d.o.o. Pukovac was used. The company "Jugo - Impex" E.E.R. d.o.o. from Niš deals with collection and recycling of cathode ray tubes of scrapped TV sets and computer monitors. The recycling center granted a certain amount of cathode ray tube glass for the purposes of this research, and the glass was further processed and milled in the Laboratory of building materials *[9].*

Table 3. Fresh mortar test results *[9]*

Fresh mortar	Mortar mark				
	E	WG25	WG50	WG75	WG100
Consistency [mm]	130	145	160	170	175
Entrained air [%]	5	5,4	4,8	4,6	5,0
Density [kg/m^3]	2265	2305	2345	2383	2396

Table 4. Flexural and compressive strengths of the mortar at the age of 2, 7, 28 and 90 days [9]

Type of mortar	Age [days]							
	2		7		28		90	
	f_s [MPa]	f_p [MPa]	f_s [MPa]	f_p [MPa]	f_s [MPa]	f_p [MPa]	f_s [MPa]	f_p [MPa]
E	5,6	27,5	7,9	46,3	8,4	55,3	9,3	62,8
WG25	6,0	29,8	7,3	43,6	8,1	57,2	8,1	62,5
WG50	5,9	30,6	7,5	44,9	7,6	57,1	6,8	64,7
WG75	5,8	29,6	6,4	45,7	7,0	51,8	6,0	62,8
WG100	5,9	29,6	5,9	41,6	6,0	49,2	5,9	59,3

For the purpose of testing the effects of replacement of river fine aggregate by a corresponding aggregate made of recycled glass, five different mortar mixtures were made. The ratio of cement (m_c) and sand (m_p) was constant and it was $m_c : m_p = 1 : 3$. Water/cement ration was also constant and amounted to 0,5. The reference mortar (E) was made with fine river aggregate only, while the other four mortars contained a varying 25%, 50%, 75% and 100% share of replacement glass. The replacement of river aggregate by recycled glass was performed by volume. The mortar mixtures obtained their marks according to their replacement share: WG25, WG50, WG75 and WG100. Table 3 provides the results of consistency testing (slump flow test according to SRPS B.C8.042), entrained air content (according to SRPS B.C8.050) and the density of fresh compacted mortar (according to SRPS ISO 6276) *[9]*. Compressive and flexural strengths were tested at the ages of 2, 7, 28 and 90 days according to SRPS EN 196-1. The test results are displayed in table 4.

DISCUSSION OF THE RESULTS

On the basis of the results presented in the papers [7-9] it was determined that glass has effects on the consistency of the mortar; the higher the share of the glass the higher the spread diameter in the slump flow test. Regarding the well known fact that glass does not absorb water, as opposed to natural aggregate, the increase of the share of glass in past gives rise to an increased amount of water in cement mortar. Entrained air content did not noticeably change with the increase of the glass share [9]. Testing of the fresh mortar density in the papers [7] and [9] established that the increase of glass replacement share causes the increase of density. CRT glass has a higher density than fine natural aggregate, which can explain such effect of CRT glass on the mortar density. On the basis of the results presented in the paper [9] it was determined that the increase of density in comparison with the reference batch is 2% for the batch WG25 and up to 6% for the batch WG100.

The results of the compressive and flexural strengths are slightly different in the presented researches. According to the results presented in the paper [7] it was determined that with the increase of the replacement share of recycled CRT glass causes an increase of compressive and flexural strengths. The authors provided two possible explanations for such a phenomenon. The first explanation would be that the replacement of the aggregate with the recycled glass improved the aggregate packing. The other explanation is that the presence of CRT aggregate in mortar accelerates cement hydration. Also, in figure 3, it can be seen that while retaining the same shares of replacement glass instead of aggregate in the mortar at the age of 7 and 28 days, those mortar mixtures containing 25% of granulated slag have higher strengths in comparison to the mixtures with 25% of fly ash. On the other hand, at the mortar age of 90 days, the compressive strengths of the batches with different mineral admixtures become practically equal. In the paper [9] as well, the values of compressive strength increase in time, as expected, and they are fairly uniform for the corresponding age, table 4. At the age of 2 days, compressive strength ranges between 27,5 N/mm^2 and 30,6 N/mm^2, at the age of 7 it ranges between 41,6 N/mm^2 and 46,3 N/mm^2, at the age of 28 days the range is between 49,2 N/mm^2 and 57,1 N/mm^2 and at the age of 90 days, between 59,3 N/mm^2

and 64,7 N/mm^2. The relative difference of the lowest and the highest value of compressive strength, flexural strength, except at the age of 2 days decrease as the glass share in the mortar increases, table 2. Such trend should be explained by the microstructure of the mortar, or, more precisely by the quality of the realized bond of the aggregate and hardened cement mortar – transit zone.

CONCLUSION

On the basis of the results presented in the papers [7-9] several conclusions can be made when it comes to the effects of CRT aggregate on the properties of fresh and hardened mortar. With the increase of the share of CRT glass aggregate instead of fine natural aggregate, the mortar spread diameter increases.

The density of fresh compacted mortar increases with the increase of the glass share in the mortar mixture.

Compressive strength increases with the increase of mortar age. At the age of 90 days, the paper [7] determined that the highest strengths were recorded in the mortar batches which had the highest percentage of glass replacement share, while in the paper [9] a slight decrease of strength at the same age for the highest share of replacement was determined. Certainly, mortar compressive strength has a considerable value and facilitates usage of mortars in practice.

Flexural strength in the paper [8] does not change considerably for the varying percentage of glass admixture, while in the paper [9] it was determined that this strength decreases as the glass share increases.

One of the most important conclusions is that the recycled glass of cathode screens can be successfully used as a replacement for a portion of natural aggregate in mortar. In this way, a huge global environmental problem can be mitigated, and perhaps fully resolved. In order to determine an optimum percentage of replacement of aggregate by using CRT glass instead, it is necessary to perform some tests of mortar durability, the most important being: investigation of potentially dangerous alkali-silicate reaction (ASR) and possible leaching of lead of the mortars which had the funnel glass added.

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REFERENCES

1. Baldé P., Wang F., Kuehr R., Huisman J. (2015): "*The global e-waste monitor – 2014*", United Nations University, IAS – SCYCLE, Bonn, Germany.

2. Socolof M., Overly J., Geibig J. (2005): "*Envinonmental life-cycle impacts of CRT and LCD desktop computer displays*", Journal of Cleaner Production, Volume 13, Issues 13–14, Pages 1281-1294.
3. https://www.recyclingtoday.com/An Analysis of the Demand for CRT Glass Processing in the U.S.
4. Wanhua Y. (2008): "*Regulating Electrical and Electronic Wastes in China*", Review of European Community & International Environmental Law, Volume 17, Issue 3, Pages 335-344.
5. Narendra Singh, Jinhui Li, Xianlai Zeng (2016): „*Global responses for recycling waste CRTs in e- waste*", Waste Management, Volume 57, Pages 187-197.
6. Andreola F., Barbieri L., Corradi A., Lancellotti I. (2007)*: "CRT glass state of the art: A case study: Recycling in ceramic glazes",* Journal of the European Ceramic Society, Volume 27, Issues 2–3, Pages 1623-1629.
7. Zhao H., Poon C., Ling T. (2013): *"Properties of mortar prepared with recycled cathode ray tube funnel glass sand at different mineral admixture",* Construction and Building Materials, Volume 40, Pages 951-960.
8. Zhao H., Wei S. (2011): *"Study of properties of mortar containing cathode ray tubes (CRT) glass as replacement for river sand fine aggregate",* Construction and Building Materials, Volume 25, Issue 10, Pages 4059-4064.
9. Grdić D., Ristić N., Topličić – Ćurčić G., Protić M., Marinković S. (2014): *"Impact of replacement of natural aggregate with the recycled glass obtained from cathode tubes on the change of cement mortar properties",* International symposium on researching and application of modern contemporary achievements in civil engineering in the field of materials and structures, DIMKS, XXVI Congress, Vrnjačka banja, p.p. 79 – 88.

THE POTENTIAL OF *Aspergillus niger* IN BIODEGRADATION/BIOREMEDIATION OF ETHOXYLATED OLEYL-CETYL ALCOHOL

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ABSTRACT

This study was investigated the effect of 0.5% EOCA (Henkel, Serbia) on the growth and metabolic activity of *Aspergillus niger*. Changes in chemical and biochemical parameters: pH value, organic acids and biomass dry weight were observed during fungal growth for 19 days. The capacity of fungus to decrease concentration of pollutant in medium was determined at 19th day. The pollutant was influence on increase in pH value of medium but decrease in organic acids excretion and biomass production of *A. niger*. The biodegradation capacity of fungus was about 83%. The obtained results indicate on potential application of fungus in bioremediation.

Key words: Biomass, biodegradation, ethoxylated oleyl-cetyl alcohol, organic acids, pH.

INTRODUCTION

Ethoxylated oleyl-cetyl alcohol (EOCA) is non-ionic surfactant from the group of fatty alcohol ethoxylates (FAEs), which has application in various industries (detergents, household cleaners, shampoos, paper, oil, agriculture, pharmaceuticals) (1). The increase in industrial production and consumption of these active substances makes them one of the leading pollutants of the environment. After use, the residues of surfactant and their degradation products falling due to the wastewater treatment plants (WWTP) or directly on the surface of the water and sediments (2). Numerous studies have confirmed a high level of primary and total biodegradability of these surfactants in the environment. Alcohol ethoxylates (AEs) are broken down by biological treatment in WWTP, in a high percentage (95-99%) (3,4). The concentration of total AEs in effluents varied in interval 1-23 µg/L in Europe, Canada and the USA. Also, the study estimates the risk AEs for the environment is carried out continuously since the 70s until today (5,6). Toxicity for aquatic organisms, expressed as the EC_{50} varies from very toxic (<1 mg/L) to very dangerous (10-100 mg/L). Simultaneously with aforementioned studies, the studies concerning understanding of the mechanism for biodegradation of AEs in the presence of complex microbial communities have been carried out using various methods.

Bioremediation is an attractive technology that utilizes the metabolic potential of microorganisms in order to clean up the environmental pollutants to the less hazardous or non-hazardous forms with less input of chemicals, energy and time (7,8). During last two decades, many mycologists have tried the use of various fungal species in the degradation of organic compounds. Some of the best known fungi species used as mycoremediators are: *Pleurotus ostreatus*, *Rhizopus arrhizus*, *Phanerochaete chrysosporium*, *etc.,* (9).

The key to mycoremediation is determining the right fungal species to target a specific pollutant. Thus, isolation and identification of fungi from environment that are resistant to the presence of high concentrations of pollutants on the one hand, and the effect of pollutants on their metabolism on the other hand, are crucial parameters for the application of fungi in mycoremediation. The occurrence of different fungal genera in sewage and industrial wastewater and sewage sludge is well documented. However, despite of that fungi have not yet been significantly exploited for mycoremediation of such polluted environments. More extensive research needs to be carried out on the use of fungi in mycoremediation.

The current study was designated with aim to investigate and promote the potential of *A. niger* in bioremediation of wastewater from AEs.

MATERIALS AND METHODS

Isolation and identification of the fungus from wastewater. Pure culture of *A. niger* van Tieghem (1867) was isolated from wastewater samples of Lepenica river basin (Kragujevac, Serbia) at a place where municipal wastewater discharge into the river. Identification of the fungus was based on the macroscopic and microscopic morphology by using Systematic key (10) and carried out at the Faculty of Biology, University of Belgrade, Serbia. The fungus was cultivated on potato dextrose agar (PDA, Sigma-Aldrich, Germani) plates at 28°C for 5-7 days until sporulation. After having sufficient population of spores, the PDA plates were stored at 4°C and sub-cultured monthly under sterile conditions.

Preparation of spore inoculum. Spore suspensions were prepared according to procedure described in our previous work (11). The concentration of spores in the suspension was evaluated by microscopic enumeration with a cell-counting hemocytometer, Neubauer chamber (Lonza Cologne AG, Germany) and adjusted to $5.0 \cdot 10^6$ spores/mL.

Culture conditions. Shake flask cultivation was carried out in 250 mL Erlenmeyer flasks containing 200 mL of Czapek-Dox liquid medium (g/L): $NaNO_3$ – 3.0, K_2HPO_4 – 1.0, $MgSO_4 \cdot 7H_2O$ – 0.25, $FeSO_4 \cdot 7H_2O$ – 0.01, sucrose – 30.0 (control – C). The same medium was supplemented with 0.5% EOCA (Henkel, Serbia) (medium EOCA). The pH value of C medium was about 6.8±0.2 (without adjustment) before sterilization. Thereafter, 1 mL of spore suspension (5.0×10^6 spores) was inoculated in liquid media. Inoculated flasks were incubated at 150 *rpm* on a shaker (Kinetor-m, Slovenia) and ambient temperature (28°C±3°C) for 19 days in triplicate. The mycelium was collected by filtration of fermentation broth using Whatman No.1 (Germany) filter paper at 19th day.

Determination of dry weight biomass (DW). The fungal biomass DW produced in C and EOCA media was determined gravimetrically according to standard procedure (11). The obtained results were expressed in g/L of submerged culture.

Determination of concentration of non-ionic surfactant (NS) in medium. To investigate the biodegradation capacity of the tested fungi, NS concentration in fermentation broth of fungi was measured by cobalt thiocyanate active substances (CTAS) method. Fermentation broth of fungi was extracted sequentially with ethyl acetate, according to procedure described by Traczyk *et al.,* (12). The reaction of NS with cobalt thiocyanate reagent forming Co-complex in which cobalt concentration is determined at OD_{620}. Triton X-100 (Sigma-Aldrich, USA) was used as a standard for preparation of calibration curve. The percentage of the NS degradation was calculated using Eq. (1):

$$\%\ \text{Degradation} = 100 - [(\text{OD620 exp} - \text{OD620 blank}) / \text{OD620 std}] \times 100 \qquad (1),$$

where $OD_{620\ exp}$ is optical density of test sample, $OD_{620\ blank}$ is optical density of blank sample and $OD_{620\ std}$ is optical density of standard sample at 620 nm.

Measurement of pH values. A pH value of the fermentation broth was measured by pH meter (type MA-5705, Iskra, Slovenia) at 4th, 7th, 10th, 14th and 19th day of fungal growth.

Determination of free (FOA) and total (TOA) organic acids. The quantities of FOA and TOA were determined by ion exchange chromatography method according to Bullen *et al.*, (13) as described in detail in our previous paper (11). To determinate concentrations of FOA and TOA, 10 or 25 mL aliquots of ethanolic extracts of fermentation broth were sampled and titration was carried out with 0.1 M NaOH. Phenolphthalein (0.1%) was used as indicator. The obtained results were presented in %.

Statistical analysis. Statistical analysis was performed using SPSS statistical software package (SPSS for Windows, ver. 13.0, Chicago, IL, USA). For tested the normality of distribution, means and standard deviation, Student *t*-test was used. Pearson's and Spearman's correlation coefficients were used for the measurement of the strength of the association between variables. All significance tests were two-tailed (0.05 and 0.01) and $p<0.05$ was considered significant.

RESULTS AND DISCUSSION

Effect of EOCA on fungal biomass DW. The biomass DW of *A. niger* measured in C and EOCA media at 19th day of cultivation was presented in Fig. 1(*a*). The slightly higher biomass was produced by *A. niger* in C (2.17 g/L) than in EOCA medium (1.98 g/L). On the other words, the addition of EOCA in growth medium caused slight inhibitory effect (8.5%) on the fungal growth compared to control. Overview of literature provides evidence that NS can both stimulate and inhibit the fungal growth, depending on fungal species and concentration of pollutant. The study of Zeng *et al.,* (14) found that Tween 80 has a mild stimulating effect on biomass of *Penicillium simplicissimum*. Stojanović *et al.,* (15,16) revealed a mild stimulatory and very strong inhibitory effect of 1% EOCA on biomasses of *Trichothecium roseum* and *A. niger,* respectively. Our previous work (17) showed a mild stimulatory effect of aforementioned types of surfactant at a concentration of 0.1% on the production of *Fusarium oxysporum.* The results aforementioned confirmed that the effect of surfactants on the growth and metabolism of fungi is very complex. This phenomenon could be explained by the interaction of the surfactant with functional groups in fungal membranes, influence on rheological properties and pH value of medium, oxygen uptake, and on active centers of the key enzymes of fungal metabolism.

Biodegradation assay of EOCA. The result of the biodegradation ability of *A. niger* grown in liquid medium with EOCA are presented in Fig. 1(*b*). CTAS assay used for determination of EOCA concentration in inoculated medium confirmed the significant biodegradation potential of the fungus. After 19 days of cultivation, the concentration of EOCA in medium decreased from initial value of 5.0 to 0.85 mg/mL. Expressed in percentages, about 83% of EOCA was removed from medium as result of metabolic activity of *A. niger*. Only a few data about biodegradation of NS by single microorganisms, especially by fungi can be found in the literature. The study of Mohamed *et al.,* (2014) confirmed the degradation of naphthalene by *A. niger* isolated from soil of petroleum refinery. According to this study, under the optimal conditions (pH 7.0, concentration of naphthalene 100 ppm and temperature 30°C), *A. niger* degraded 87.90% of naphthalene after 8 days. Recently, Jakovljević and Vrvić (19) revealed that *A. niger* decomposed about 30% of AS (components of commercial detergent Merix, Henkel, Serbia) after 16 days of incubation. The current result confirmed that *A. niger* is about 2.7-fold more efficient in biodegradation of NS than AS. These result is in accordance with conclusion of Jurado *et al.,* (20) that biodegradation of NS by *Pseudomonas putida* is much more efficient compared to AS. Jun *et al.,* (21) found that *Trichoderma viride* can ability to degrade Tween 80 up to more than 8 g/L at pH 7.0 and 20°C. The obtained results clearly show that *A. niger* could be applied in the purification of wastewater which contains detergents.

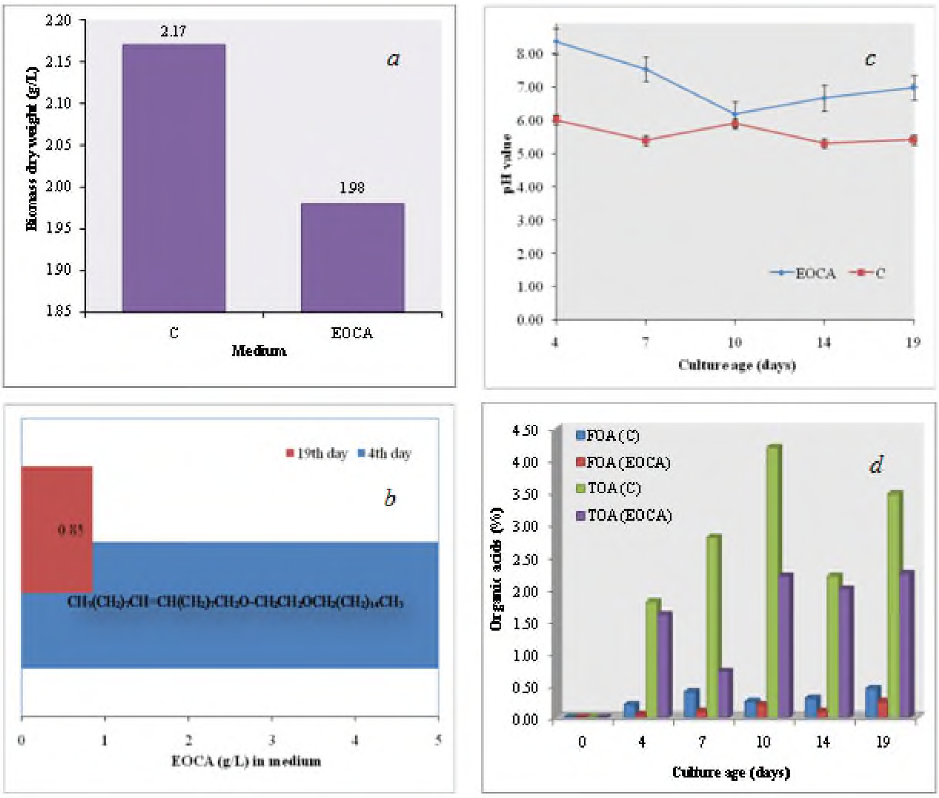

Figure 1. Display of the biochemical parameters of *Aspergillus niger* in control (C) and medium with ethoxylated oleyl-cetyl alcohol (EOCA): production of biomass dry weight (*a*); biodegradation ability (*b*); pH value (*c*); quantities of organic acids (free (FOA) and total (TOA) (*d*).

Effect of EOCA on pH of medium. The changes in pH values of C and EOCA media of *A. niger* are presented in Fig. 1(*c*). Altering pH medium is result of utilization nutrients from growth medium and excretion of some acid and alkaline metabolites by fungi (22). Thus, the intensity of pH changes is in correlation with intensity of metabolic activities of the fungus. The pH values of C medium of *A. niger* decreased continually from inoculation until 10th day and moved toward acidic condition. The most significant changes in pH were noted in first 4 days after inoculation, which means that the most significant metabolic changes are associated with spores germination and mycelial growth. Afterwards, the only increase in pH values was noted at 14th day, probably as a result of autolysis and excretion of alkaline metabolites. Addition of EOCA in medium caused a significant increase in initial pH value (8.50 units) compared to C, and, thus, this compound can be considered as factor of alkaline stress. As respond to alkaline stress the fungus excreted organic acids, due to the pH value of medium was considerable decreasing until 10th day. From this point, the pH value of medium was increasing until 19th day. Statistical analysis revealed a negative correlation between changes in pH values and quantities of FOA (r = -0.830, $p < 0.01$) and TOA (r = -0.707, $p < 0.05$). The decrease of media pH values by fungi during treatment of sludge was observed and well discussed by several authors (27, 28).

Effect of pollutant on quantity of organic acids (FOA and TOA). The fungus excreted variable amounts of organic acids in the liquid media, depending on medium composition and a period of cultivation (Fig. 1(*d*)). The quantity of FOA produced in C and EOCA media by *A. niger* ranged from 0.20% to 0.45% and 0.05% to 0.25% respectively. The quantity of TOA measured in C and EOCA media was 1.80% to 4.20% and 0.70% to 2.20% respectively. Based on presented results, the EOCA caused an inhibitory effect on quantity of FOA (44.4%) and TOA (47.6%) compared to control. Statistical data revealed strong correlation between quantities of FOA and TOA (r = 0.873, $p < 0.01$) in EOCA medium. The quantities of FOA and TOA excreted in medium were correlated with duration of experiment (r = 0.705, $p < 0.05$ and r = 0.664, $p < 0.05$, respectively). These results are in agreement with literature data about capability of *Aspergillus* genus to produce high amounts of useful organic acids (citric, gluconic, malic, itaconic acids) (23). The growth of fungus expressed as biomass DW was correlated with quantity of TOA (r = 0.973, $p < 0.05$). The correlation between biomass and quantity of TOA was also found in our previous biodegradation study with *Penicillium chrysogenum* (11). Briefly, the quantity of excreted TOA depends on the fungal growth and intensity of metabolic activity.

CONCLUSIONS

During fungal growth in Czapek-Dox liquid media supplemented with EOCA at a concentration of 0.5%, the total 83% of pollutant was removed by *A. niger* for 19 days. The obtained results indicate the potential application of tested fungus in wastewater treatment, detergent industry and biotechnology.

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REFERENCES

1. Jakovljević, V., Vrvić, M., (2015). Potencijalna uloga gljive *Alternaria tenuis* u bioremedijaciji ekosistema kontaminiranih etoksilovanim alkoholom. Skup, 7(2): Zbornik radova III Simpozijuma biologa i ekologa Republike Srpske (SBERS 2015) II Banja Luka, 12-14. novembar 2015. Prirodno-matematicki fakultet Univerziteta u Banjoj Luci, 2016.

2. Odds, F.C., Brown A.J., Gow N.A., (2004). *Candida albicans* genome sequence: A platform for genomics in the absence of genetics. Genome Biol., 5(7): 230.
3. Ali, T.A., Wainwright, A.M., (1994). Growth of *Phanerochaete chrysosporium* in soil and its ability to degrade the fungicide benomyl. Biores.Technol., 49(3): 197-201.
4. Jeon, C.O., Madsen E.L. (2012). *In situ* microbial metabolism of aromatic-hydrocarbon environmental pollutants. Curr. Opin. Biotechnol., 24(1): 1–8.
5. Ying, G.G., (2006). Fate, behavior and effects of surfactants and their degradation products in the environment. Environ. Int., 32(3): 417–431.
6. Human and Environmental Risk Assessments (HERA) (2009). Alcohol ethoxylates (AE) human and environmental risk assessment. http://www.heraproject.com.
7. Asgher, M., Bhatti, H.N., Ashraf, M., Legge, R.L., (2008). Recent developments in biodegradation of industrial pollutants by whiterot fungi and their enzyme system. Biodegradation, 19(6):771-83.
8. Haritash, A.K., Kaushik, C.P., (2009). Biodegradation aspects of polycyclic aromatic hydrocarbons of polycyclic aromatic hydrocarbons (PAHs). A review. J. Hazardous Materials, 169(1-3); 1-15.
9. Thakur, M., (2014). Mycoremediation - a potential tool to control soil pollution. Asian J. Environ. Sci., 9(1): 24-31.
10. Raper, K.B., Fennell, D.I., (1965). *The genus Aspergillus*, Baltimore MD, Maryland: Williams and Wilkins.
11. Jakovljević, V., Milićević, J., Stojanović, J., (2014). Detergent-like stressor and nutrient in metabolism of *Penicillium chrysogenum.* Biotechnol. Biotec. Eq., 28(1): 43-51.
12. Traczyk, L., Szymanski, A., Wyrwas, B., Jaroszynski, T., Lukaszewski, Z., (2006). Efficiency of Non-Ionic Surfactant Removal in Biological Sewage Treatment Plants. Polish J. Environ. Stud., 15(3): 493-499.
13. Bulen, W.A., Varner, J.E., Burrell, R.C., (1952). Separation of Organic Acids from Plant Tissues. Anal. Chem., 24(1): 187-190.
14. Zeng, G.M., Shi, J.G, Yuan, X.Z., Liu, J., Zhang, Z.B., Huang, G.H., Li J.B., Xi B.D., Liu H.L., (2006). Effects of Tween 80 and rhamnolipid on the extracellular enzymes of *Penicillium simplicissimum* isolated from compost. Enzyme Microb. Technol., 39(7): 1451-1456.
15. Stojanović, J., Jakovljević, V., Matović, I., Gajović, O., Mijušković, Z., Nedeljković, T., (2011). Influence of detergent on metabolic activity of fungi *Aspergillus niger*. Natural Science 3(6): 466-470.
16. Stojanović, J., Milićević, J., Gajović, O., Jakovljević, V., Matović, I., Mijušković, Z., Nedeljković, T., (2011). The effects of detergent, sodium tripoly-phosphate and ethoxyled oleylcetyl at metabolic parameters of the fungus *Trichothecium roseum* Link. Arch. Biol. Sci. Belgrade, 63(4): 1001-1006.

17. Jakovljević, V.D., Milićević, J.M., Stojanović, J.D., Solujić, S.R., Vrvić, M.M., (2014). The influence of detergent and its components on metabolism of *Fusarium oxysporum* in submerged fermentation. Hem. Ind., 68(4): 465-473.
18. Mohammed, D.B., Khudeir, S.H., Al-Jubouri, M.H., (2014). The Optimum Conditions for Naphthalene Biodegradation by Filamentous Fungi. Iraqi J. Sci., 55(4B): 1780-1791.
19. Jakovljević, V.D., Vrvić, M.M., (2016). Capacity of *Aspergillus niger* to degrade anionic surfactants and coproduce the detergent compatible enzymes. Appl. Biochem. Microbiol., 52(2): 183-189.
20. Jurado, E., Fernández-Serrano, M., Ríos, F., Lechuga, M., (2013). Aerobic Biodegradation of Surfactants. In: Chamy, R. and Rosenkranz, F., Eds. *Biodegradation-Life of Science*, pp. 63-81, InTechOpen, Rijeka.
21. Jakovljević, V., (2016). Metabolic activity of *Aspergillus niger* and *Fusarium lateritium* induced by ethoxylated oleyl cetyl alcohol and their bioremediation and biotechnological potential. Appl. Biochem. Microbiol., 52(4): 406-412.
22. Orlowski, M., (1991). *Mucor* dimorphism. Microbiol. Rev., 55(2): 234-258.
23. Li, A., Punt, P., (2013). Industrial production of organic acids by fungi: State of the art and opportunities. In: Gupta, V., Schmill, M., Mazutti, M., Mäki, M., Tuohy, M., Eds., *Applications of Microbial Engineering,* pp. 52-74. Taylor and Francis Group, London.

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POSSIBILITIES OF THE PLASMA TECHNOLOGY APPLICATION FOR WASTE TREATMENT IN METAL PROCESSING INDUSTRY

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ABSTRACT

This paper discusses one of the areas from the list of important national needs – the use of waste for energy production. This problem affects every resident, involves over one million employees, occupies millions of of hectares of land, generates many environmental problems and becomes one of the major challenges of the 21st century. Today it's a problem awaiting a good solution everywhere even on the territory of Northern Kosovo. The application of plasma technology represents a completely new approach to the treatment of waste, particularly important in terms of sustainable development and global warming. In addition to the general considerations of possible use of plasma technology in the treatment of industrial waste, the paper suggests feasible and technically correct solutions for waste treatment in metal processing plants on the territory of Northern Kosovo.

Key word: Remediation of waste, Plasma system, Plasma Torch, Syngas.

INTRODUCTION

The world applies different technologies for the treatment and remediation of waste, and continuously working on the development of new and improve existing processes. All applied technologies differ from each other by a medium, on which they can be applied, according to the pollutants which are removed, according to the efficiency and cost per unit of processed medium and according to the duration time of the remediation. Due to the presence of volatile organic compounds, as well as some inorganic substances, whose extraction is usually the consequence of a change of pH value, during the remediation of waste, often lead to the emission of hazardous substances that are a source of air pollution. Remediation technologies often can be the cause of further spread of contamination, which should be taken into account, and should take all measures to prevent such occurrences.

In the developed Europe countries and especially the USA, in the last 15 years there has been a rapid development of application of thermal plasma in degradation, first hazardous, and then the industrial and municipal waste. The rapid development of plasma technology,, first for the military needs and later for civilian applications, caused a significant reduction in the prices of complete systems, as well as lowering the price of waste treatment in them. In other words, plasma technology, in terms of costs, become competitive with other technologies both in sense of the investment and in sense of the exploitation. It especially relates to the thermal treatment of waste such as high-temperature combustion – incineration. [1-3].

Incineration is the process of reducing the volume of waste by burning and energy production from this process. But burning of the waste produces a strong emission of carbon dioxide, water vapor and toxic gases (EPA research on dioxin), whose composition depends on the composition of the waste. As is well known, carbon dioxide is one of the causes of global warming of our planet. Therefore, the world is increasingly turning to the application of plasma processes, which are now commercially used, not only for the treatment of hazardous and nuclear, but also for the industrial and municipal waste.

Investments in the plasma system of the same capacity as for the incinerator are approximately 15% lower. If we take into account that the incinerator ash can be the "hazardous waste" (which is then sometimes treated by plasma system), it is clear that the plasma technology today is more competitive in relation to the incineration of hazardous waste. Plasma system represents a modern and unique technology of waste treatment, that is completely environmentally friendly. In this kind of treatment one of the main products is slag, a non-crystalline, glassy mass, which incorporates all inorganic substances and does not allow them to leaching. Slag can be comminuted and, as crushed or ground aggregate, used for different purposes. The second product of waste treatment is a plasma gas, which, when purified in the system, that is the part of the plasma plant, represents the very calorific fuel consisting of hydrogen and carbon monoxide. If the metal component is present in the waste, it has a characteristic to separate of the slag and separately discharge from the system. Such a treatment of waste, using plasma converter, is called gasification and vitrification. To what extent is this method safe and environmentally friendly shows the fact that the plasma treatment of waste is officially approved for the treatment of low level radioactive waste, wherein the vitreous slag can be disposed even in the ordinary landfill sites.[2].

Industrial waste management, the collection, treatment and disposal of the waste, pose a particular problem in Northern Kosovo and Metohija. In the context of this issue, we discussed the possibilities for the treatment of industrial waste which is generated in the factory for the production of steel forgings, *FOT* in Leshak and in the mine and flotation plant *Trepca - Kopaonik* in Leposavic. We especially discussed the problem of soil contamination and remediation of slag dumps and tailing ponds. Long-term exploitation of lead-zinc ore in the mine and flotation plant Trepca - Leposavic, as well as the uncontrolled disposal of tailing, slag and other waste has polluted the basic structure of the soil, and the presence of heavy metals, which can remain in the soil many years, requires remediation with which their concentration will be reduced to the acceptable or permissible value.

OBJECTIVES AND CONTENT OF THE RESEARCH

The aim of this paper is to consider the possibilities of treatment of industrial waste that is generated in plants *FOT* in Leshak and *MIF Trepca - Kopaonik* in Leposavic using thermal plasma. Figure 1 shows the effusion of contaminated water from the mine Zuta Prlina that belongs to *MIF Trepca - Kopaonik*, and Figure 2. shows the deposits of arsenic trioxide in the tailings Gornji Krnjin and Bostaniste in the municipality of Leposavic.

Figure 1. Inflow of waste water of Zuta Prlina mine into Leposavska River

Figure 2. Arsenic trioxide on the tailings Gornji Krnjin and Bostaniste

The waste that is generated in the blacksmith shop, mechanical processing, heat treatment and non-production units of the factory *FOT* has a somewhat similar composition as municipal solid waste but with higher content of heavy metals, especially iron. In addition,, the waste contains wooden and polyethylene packaging, paper, solid kitchen waste, garbage from the offices, etc. The total amount of generated waste is approx. 20 - 25 tons per month.

Waste from flotation and from the mine in Leposavic contains mainly flotation tailings which has a high percentage of toxic components, the compounds of arsenic, cadmium, lead, mercury and other heavy non-ferrous metals. The average content of heavy metals in the tailings is presented in Table 1.

Table 1. The average content of heavy metals in the tailings

Component	Fe (%)	Pb (%)	Cd (ppm)	Hg (ppm)	Zn (%)	Mn (%)
Content	20-32	0,2-0,7	50-340	10-15	0,3-0,5	0,7-2,4

Plasma technology for the treatment of industrial solid waste means that the solid waste is heated to a high temperature, 5,000 to 15,000°C. The waste material enters the chamber, and the intense heat of the plasma arc breaks down the organic molecules on their elementary atoms. In a carefully controlled process these atoms recombine into hydrogen-rich gas, called syngas, whicht has a very high calorific value. Solid inorganic components of the waste such as metal and glass, immediately melt, and then vitrificate, forming a material similar to cooled lava, in which is encapsulated heavy and possibly toxic metals. In plasma technology there is no incineration, burning or even ash formation. There are two basic types of termal plasma processes: Plasma Arc (DC melter) and Plasma Torch.

Plasma Arc reactors have a very high decomposition efficiency of the components and the waste can be treated with minimal pre-treatment or even without it. Compensation of carbon electrode wear is done automatically and it allows continuous work of the reactor. It is often used for treatment of organic waste because the high temperatures produced by the arc, easily degrade organic compounds on the basic elements.

In Plasma Torch systems, arc is established between the copper electrode and the molten slag or between and copper electrode and the other electrode with the opposite polarity. As well as the Plasma Arc, the Plasma Torch systems have very high efficiency of dissociation of the components, they are very robust and suitable for the treatment of industrial waste.

Detailed analysis of the existing plasma technology for the treatment of industrial waste have demonstrated their advantage compared to the incineration and indicate possibilities for further development and extension of application fields [5-8]. Chart drive for waste treatment, and a plasma gasification is given in Figures 3 and 4.

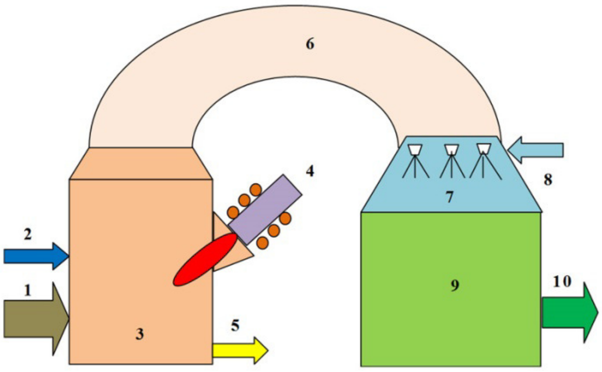

Figure 3. Scheme of the plant tor oxygen plasma gasification of waste
1 - Charging of waste; 2- Oxygen supply; 3 - Gasifier; 4 - Plasma Torch; 5 - Slag discharging; 6 - Syngas exit; 7- Vapor injector 8- Water entry; 9- Catalytic converter of vapor;10 - Syngas output

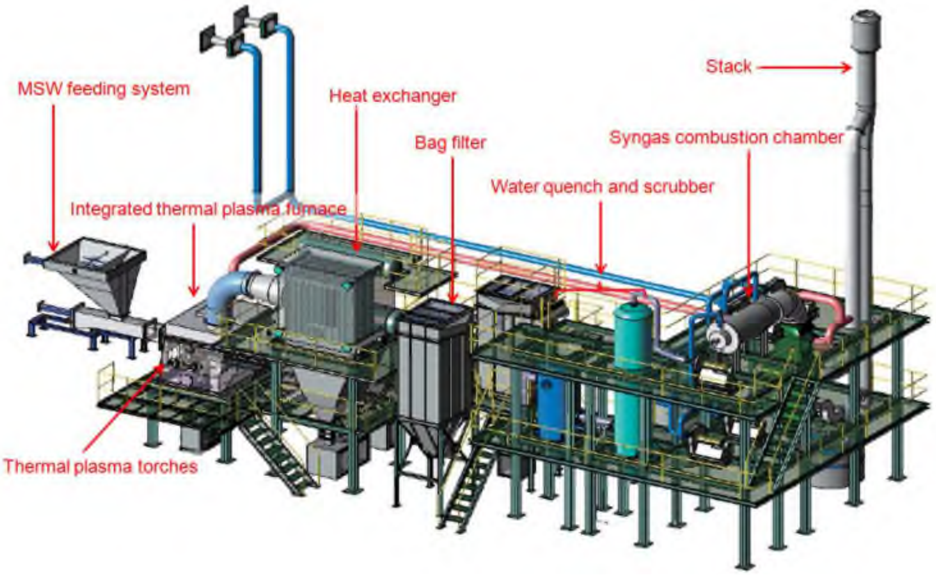

Figure 4. Plasma system for waste treatment and the production of syngas

Most of the wastes contain a large number of different hydrocarbons and other organic compounds Treatment of the waste in a special reactor - the plasma converter, is safe and environment friendly process that preserves the environment, and the final product, hydrogen-rich syngas enhances the energy efficiency of the process.

Converter has the form like a steel troughs, which is inside lined with refractory material. In the converter is carried out the process of waste disintegration. It is the endothermic process and therefore it is necessary to add energy to the batch. The plasma creates an extremely high temperature, up to 15.000°C, which leads to the dissociation of organic molecules and creates the syngas. Syngas consists mainly of hydrogen and carbon monoxide so it has a very high calorific value. This, the energy-rich gas, is commonly used to produce electricity and heat, and can also be used as a fuel in internal combustion engines.

Besides the syngas, in the plasma processing of waste, two more products are obtained. In the reactor is formed a layer of molten metal or molten metal alloy on which floats a layer of viscous slag consisting of oxides and silicates. When poured from the furnace metal alloy can be further processed and refined into standard technical alloys. Slag is also discharged from the furnace, and after the solidification and cooling it becomes chemically very stable vitreous mixture of oxides and silicates, which do not pollute the environment.

Overheated syngas (SKG) coming out of the reactor and passes through the heat exchanger to overheat the water vapor that is used to generate electricity. Syngas is maintained at sufficiently high temperature to prevent the formation of dioxins and furans. It can be used for propelling of power gas turbines and for heating the steam boilers. Plasma converter produces enough electricity to cover the operation of the plant, and the excess energy can be sold on the market. In principle, converter consumes 1/3 of produced electricity for their own needs, and the other 2/3 remain available and can be used for different purposes, sale, supply of other technological lines in the system, etc.

The construction of the plasma converter allow a simultaneous intake of solid, liquid and gaseous waste. However it should be noted that most often comes to solid waste or mixture of solid and liquid waste. The whole system operates at a low underpressure, so that emission into the environment is not possible.

Besides the conventional thermal plasma generator for the treatment of the waste, the hybrid type plasma generator which has a very long lifetime is used. Hybrid plasma generator uses a combination of radio-frequency (RF) and unidirectional (DC) module with a reverse vortex stabilized plasma. Generator uses semiconductor power sources, and plasma system is designed so that it does not use electrodes and can run thousands of hours continuously and maintenance-free [5-6].

Reached level of the power electronics allows supply of the generator up to the installed power of 1.8 MW per unit [2]. Switching from air to oxygen drastically reduces power consumption and improves the volumetric and gravimetric parameters of the whole system of gasification. Thereby, the increase in the cost is about 0,2 euros per kilogram of used oxygen, and the total production of electricity reaches 1.9 MWh per ton of municipal solid wastes or industrial wastes of appropriate quality.

RESULTS OF THE RESEARCH

In order to become more familiar with the possibilities of applying plasma in our environment, in the last three years, we made a series of experiments on equipment that could potentially be applied in Serbia. Unfortunately, we did not have representative samples of waste from industrial companies in the north of Kosovo, where the research will be the subject of a new project or technological studies. So, here we will mention some other characteristic experiments of treating waste using plasma converter.

Figure 5.a presents a sample of soil soaked with oil, taken from the oil refinery in Pancevo, and on Figure 5.b. It can be seen vitrified residue of the sample, after the plasma treatment. The total volume of the residue was about 9 vol.%.

a. **b.**

Figure 5. Sample of soil soaked with oil before (a) and after the treatment (b)

In Figure 6a was presented to a sample of medical waste, and in Figure 6.d. can be seen the residue after the plasma treatment. The total volume of the residue was less than 2 vol.%.

a. **b.**

Figure 6. A sample of medical waste before (a) and after the treatment (b)

For powering the plasma generator was used thyristor device device 100V 1000A. Control of the device is done electronically on LABVIEW platform, This plasma system is used exclusively for laboratory and pilot studies in waste treatment.

CONCLUSION

Plasma technology is without competition, the best process in waste management, because all other procedures reduce the problem, but does not solve it. The plasma process provides solving problems for all kinds of waste except strong radioactive, almost without negative impact on the environment and human health, and with the lowest price of treatment per ton.

Clean and efficient processing of industrial waste and its conversion to any type of energy. represents a serious global problem that affects all of humanity. Development and implementation of technologies for future generations, which include plasma technology, should be the challenge of our generation.

The problem waste treatment in industrial enterprises such as *FOT*, Leshak and *Trepca - Kopaonik*, Leposavic, can be completely solved by applying a plasma plant of suitable capacity. Moreover, plasma plants of higher capacity can be used for remediation of tailings which would definitely solve the problem of pollution of soil and water flows.

REFERENCES

1. Themelis N. J, (2003) "An overview of the global waste-to-energy industry", Waste Management World - Review Issue, July-August 2003, p. 40-47.
2. Čikara D, Minić D, Rakin P, Rakin D, (2010) „Modern Plasma Technology for recycling of Waste Materialas and turning Waste into Energy", Conference of Modern Technologies and Biotechnologies for Environmental Protection, Sibiu, Romania - Proceedings pp 25-31.
3. Carabin, P., Gagnon, J-R. (2007) "Plasma Gasification and Vitrification of Ash-Conversion of Ash into Glass-like Products and Syngas", World of Coal Ash (WOCA), Covington, Kentucky, pp. 1-11.
4. Živković B. (2014) "Tretman otpada plazma tehnologijom", Limes plus, 1/2014, pp. 77-86, Hesperia edu, Beograd
5. Matveev, I.B., Serbin, S.I., Lux, S.M. (2008) "Efficiency of a Hybrid-Type Plasma-Assisted Fuel Reformation System", *IEEE Trans. Plasma Sci.* 36 (6), pp. 2940-2946.
6. Matveev, I.B., (2008) Applied Plasma Technologies, U.S. Patent 7,452,513 B2 "Triple Helical Flow Vortex Reactor", Nov.18, 2008.

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THE ELECTROCHEMICAL PROPERTIES OF THE BARIUM FERRATE PLASTIC-BONDED CATHODE FOR SUPER-IRON BATTERY

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ABSTRACT

The solid salts of the ferrate anion might offer significant advantages over conventional materials used as cathodes because of the three electron transfer associated with the reduction of Fe(VI) to Fe(III. In the present study, we have shown the performance of the electrochemically synthesized barium ferrate cathode. Our preliminary results demonstrate that the porous plastic bonded thin foil electrodes based on electrochemically synthesized barium ferrate can be considered in spiral wound battery geometry for higher rate capability.

Key words: Fe(VI); Super-iron battery; Electrochemically synthesized $BaFeO_4$; Thin plastic-bonded cathode; Alkaline battery; Specific capacity.

INTRODUCTION

Licht et al. [1] revealed that solid salts of the ferrate anion FeO_4^{2-} might offer significant advantages over conventional materials used as cathodes because of the three electron transfer associated with the reduction of Fe(VI) to Fe(III). The new class of batteries with a solid ferrate as a cathode, termed super-iron batteries,is divided into three types: super-iron primary alkaline battery utilizing a Zn anode, the super-iron metal hydride rechargeable alkaline battery, and super-iron rechargeable lithium non-aqueous battery. Since this initial report, several studies have investigated the three-electron reduction of Fe(VI) to Fe(III) to evaluate the suitability of ferrate materials for both alkaline and non-aqueous batteries [2-6].

A wide variety of solid ferrates have been extensively investigated as a positive electrode material for super-iron alkaline batteries. Among these ferrates, $BaFeO_4$ and K_2FeO_4 are particularly appealing since both combine attributes of very low alkaline solubility and high stability. $BaFeO_4$, although of lower intrinsic three-electron specific capacity (312.6 mAh g^{-1}) than K_2FeO_4 (406 mAh g^{-1}), is observed to support higher current densities than K_2FeO_4 [1]. Further studies have shown that at high load (current densities above 1 mA cm^{-2}) the faradaic efficiency of Fe(VI) reduction is significantly higher for a $BaFeO_4$ cathode compared to a K_2FeO_4 cathode [7]. These cathodes can be considered environmentally friendly with benign ecological discharge products.

In the present study, we have presented the performance of the plastic bonded cathode based on electrochemically synthesized barium ferrate cathode.

EXPERIMENTAL DETAILS

Solid barium ferrate was synthesized via the electrochemically synthesis of K_2FeO_4 in a two compartment electrolysis cell separated with a ceramic anion impermeable membrane [8]. The 10M potassium hydroxide solution is placed in both, the anolyte and catholyte compartments. High surface area iron anodes were prepared from transformer steel sheet (M120, EN 10106-1996, composition: 0.0075% C, 3.02%Si, 0.10% Mn, 0.027 % S, 0.006 % P, 0.035% Al, the rest being Fe). The cathode consisted of high-surface area platinum gauze. All electrolytes using in synthesis were prepared from analytical grade reagents and triply distilled water. Experiments were conducted under N_2 bubble generated convection. N_2-bubbling also eliminated the possibility of CO_2 exposure, because the presence of CO_2 in solution leads to the precipitation of a $BaCO_3$, very harmful impurity phase for the active cathode mass utilization in super iron batteries [9].The transpassive anodic dissolution was carried out for a period of 2 hours using constant current of 3 A (j < 20 $mAcm^{-2}$) controlled by PSH-2018A programmable switching DC power supply. The temperature was kept near 50 °C. The net Fe(VI) solution phase alkaline synthesis reaction is:

$$Fe + 2KOH + 2H_2O \rightarrow K_2FeO_4 + 3H_2 \qquad (1)$$

The concentration of synthesized K_2FeO_4,a purple red anolyte solution was determined by the chromite method [10]. The resultant anolyte, K_2FeO_4 solution, was removed from the electrolysis chamber and added through a filter to a 10% wt. $Ba(OH)_2$, utilizing a volume of the $Ba(OH)_2$ solution calculated according to a predetermined Ba:Fe ratio. After 10 min vigorously stirring an ex situ solid $BaFeO_4$ can be precipitated due to the low solubility compared to K_2FeO_4:

$$K_2FeO_4 + Ba(OH)_2 \rightarrow BaFeO_4 \downarrow + 2KOH \qquad (2)$$

The resultant suspension was vacuum filtered through sintered glass filter B2, and washed with chilly triply distilled water to pH7. The washed $BaFeO_4$ was dried at room temperature for 20 h under 50 mbar to a constant mass, and then kept in desiccator over silica gel under 300 mbar. $BaFeO_4$ yield and purity were *determined* by titrimetric chromite analysis[10]. The yield was 90 % of theoretical value with purity of 95%.

FTIR spectrum of $BaFeO_4$ mixed in a conventional KBr pellet was obtained by using a Bomem MB-100, Hartman and Braun spectrophotometer.

The first step in plastic bonded ferrate cathode preparation was mixing 70 wt. % $BaFeO_4$ material with 25 wt. % T-44 graphite. The powder mixture was homogenized by dry milling in a plastic vessel for 30 minutes, whereupon the*remaining* 5% PTFE binder, grade CD1, was added together with appropriate amount of isopropyl alcohol as a wetting agent and pore forming agent. A mixture was ground with a mortar and pestle to produce a homogeneous mixture, *which was then*rolled into a thick foil, approximately 1 mm. The foil afterwards was kneaded by sequential rolling and folding in order to make fibrous network that has a cohesive structure. Finally, the mass is treated by rolling into thin foil of 200 μm. The electrode was cut out of foil using a punch tool 11 mm diameter. In order to improve adherence, the electrodes were fabricated by pressing the electrode onto expanded Ni foam at about 3 MPa for 1 min. Before each test, the electrodes were soaked under vacuum in 5M KOH for 15 min.

The procedure for preparation of porous plastic bonded zinc anodes is the same as that was applied for porous plastic bonded barium ferrate cathode except that the composition in the first step was 45 wt. % Zn powder (nominal purity >98%), 50 wt. % ZnO powder (nominal purity >99%).

All the electrochemical half-cell measurements were performed using SP-150 potentiostat/galvanostat, computerized instrument from BioLogic Inc. Experiments were carried out at room temperature in an open single-compartment cell consisting of a working electrode ($BaFeO_4$ - based active material), a counter electrode (platinum gauze), a reference electrode (Hg/HgO in1M KOH), and 5M aqueous solution of KOH as electrolyte. The current densities were calculated from the geometrical surface in contact with the electrolyte. Constant-current *charge-discharge tests* at the current density of 1 mA cm^{-2} of electrodes were carried out in 5 cycles under room temperature. The cut-off potential was set at 150 mV vs. reference electrode limited the time of discharge and charging was done to a charge return of 130%. The cyclic voltammetry experiment was conducted during the second cycle at 30% depth of discharge (DOD), calculated in relation to a capacity achieved in the first cycle. The cyclic voltammetry experiment was done by scanning the potential at a rate of 100 mV s^{-1} between 150 and 700 mV versus reference electrode. A full alkaline super-iron cell ($BaFeO_4$/Zn) performance was evaluated in a coin-type stainless steel model assembled using the porous plastic bonded barium ferrate cathode and an excess of plastic bonded zinc electrode separated by a nonwoven Viledon separator (polypropylene-based membrane – Viledon FS2125) in 5M aqueous solution of KOH.

RESULTS AND DISCUSSION

Characteristic triplet of the absorbance bands of FTIR spectrum at wave numbers 856, 816, and 777 cm^{-1} for electrochemically synthesized $BaFeO_4$ showed in Figure 1 correlates well with relevant literature data for $BaFeO_4$ [11-13]. The location and magnitude of a peak observed to grow at wave number 692 cm^{-1}correlate with the FTIR absorption for pure$Ba(OH)_2 \cdot 8H_2O$. It indicates that barium hydroxide is impurity present in the synthesized $BaFeO_4$. The presence of $Ba(OH)_2$ is even desirable for use in the *alkaline super-iron batteries because*small amounts of added $Ba(OH)_2$ can constructively enhance the Fe*(*VI*)* insolubility. $BaFeO_4$ is characterized by very low solubility in a 5 M KOH solution containing saturated $Ba(OH)_2$, dissolving to less than 0.2 mM [2].

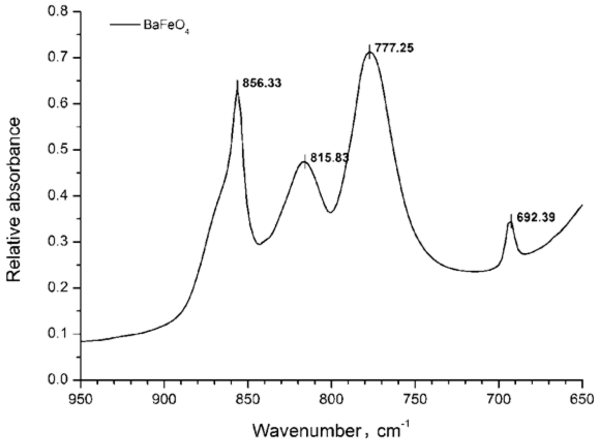

Figure 1. FTIR spectrum of electrochemically synthesized BaFeO$_4$

Figure 2 shows an initial discharge curve in the first cycle of sample at a constant current density of 1 mA cm^{-1}.The BaFeO$_4$cathode shows specific discharge capacity of 194 mAh g^{-1}. The results indicate that the BaFeO$_4$ cathode delivers the about 62% of the theoretical specific capacity for BaFeO$_4$ and gives a long plateau region above 230 mV versus Hg/HgO reference electrode. This flat discharge potential profile is characteristic of the coexistence of two distinct solid phases, Fe(VI) and Fe(III), each having a compositional stability range.

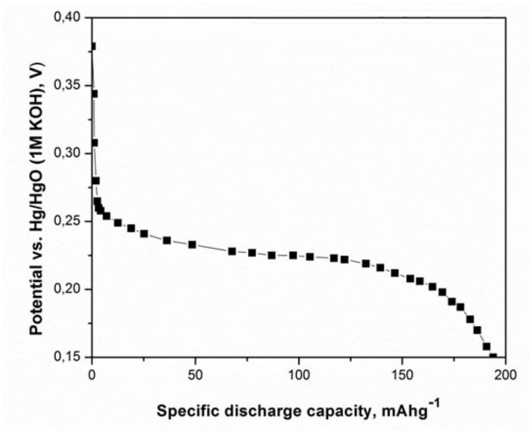

Figure 2. Initial discharge curves of the BaFeO$_4$ cathode at a rate of 1 mA cm^{-2}

Cell cycling in this study was implemented using the excess electrolyte only as a first approach because it is expected that capacity in these conditions declines rapidly with cycle number due to soluble components of the reaction dissolve into electrolyte and diffuse into the bulk electrolyte. Using an appropriate amount of electrolyte is critical to achieving a good balance between capacity and cyclability and therefore this issue *will* be a *focus* of our *future work.* The results of our cycling experiments are compiled in Table 1.

Table 1. Specific discharge capacity of the $BaFeO_4$ cathodes vs. cycle number

Cathode materials	Specific discharge capacity (mAh g^{-1}) vs. cycle number				
	1st	2nd	3rd	4th	5th
$BaFeO_4$	194	142	101	42	21

The discharge of cells is interrupted at 30% depth of discharge in the second cycle in order to run cyclic voltammetry.

The cyclic voltammogram for the porous partly discharged cathodes is presented in Figure 3. Cyclic voltammograms are established after 2–3 cycles and do not change with further cycling. One anodic oxidation peak prior to the oxygen evolution reaction starts and one cathodic reduction peak are observable on the CV curves. The redox peak can be assigned to the electron transfer process described by the following well-accepted reaction:

$$FeO_4^{2-} + \frac{5}{2}H_2O + 3e^- \rightarrow \frac{1}{2}Fe_2O_3 + 5HO^- \qquad (3)$$

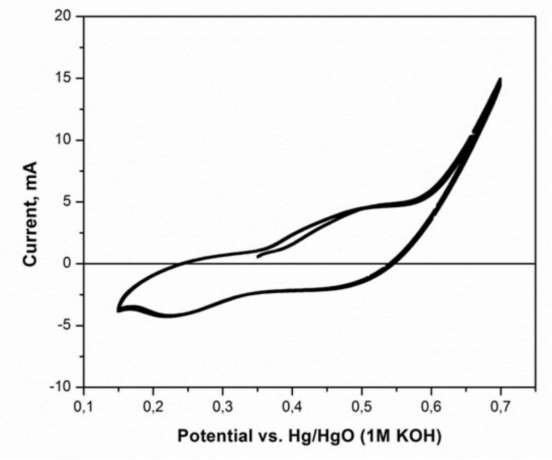

Figure 3. CV profile of the $BaFeO_4$ cathode at a scanning rate of 100 mV s^{-1} from 0.15 V to 0.7 V vs. Hg/HgO

The equilibrium potential of the ferrate(VI)/ferrate(III) redox couple obtained by adding the potential positions of the anodic and cathodic peaks and dividing by 2 is 370 mV vs. Hg/HgO.

In this study a full alkaline super-iron cell ($BaFeO_4$/Zn) is assembled so as to evaluate its electrochemical properties. The open circuit voltage is 1.84 V. In the first galvanostatic discharge, the $BaFeO_4$/Zn coin cell shows (Fig. 4) a characteristic plateau at 1.55 V and specific cell capacity of 208 mAh g^{-1}. It is in full compliance with data published earlier [5, 14].

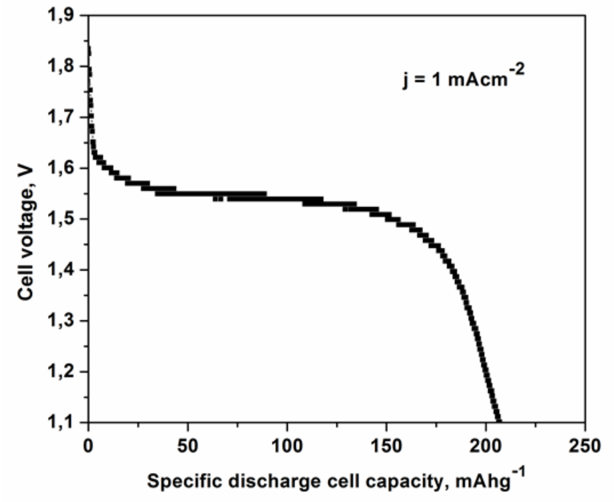

Figure 4. Typical discharge characteristic of alkaline super-iron $BaFeO_4$/Zn cell

The results in our preliminary experiments indicate that the alkaline super-iron cell ($BaFeO_4$/Zn), assembled of the porous plastic bonded thin foil electrodes makes a promising solution to the embodiment, especially if we considerthe form of a spiral wound battery geometry for higher rate capability.

CONCLUSION

This article continues the electrochemical investigation of aqueous alkaline 'super-iron' batteries, and demonstrates capabilities of plastic-bonded cathodes based on electrochemically synthesized $BaFeO_4$. Through process optimization of operating conditions and cathode material composition the electrochemical parameters of cathodes can be expected to improve. Also, our preliminary results demonstrate that the porous plastic bonded thin foil electrodes can be considered in spiral wound battery geometry for higher rate capability.

Acknowledgment

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REFERENCES

1. S. Licht, B. Wang, S. Ghosh, Science 285 (1999) 1039-1042.
2. S. Licht, B. Wang, S. Ghosh, J. Li, V. Naschitz, Electrochem. Commun.1 (1999) 522.
3. S. Licht, B. Wang, Electrochem. Solid-State Lett.3 (2000) 209.
4. S. Licht, S. Ghosh, Q. Dong, J. Electrochem. Soc. 148 (2001) A1072.
5. S. Licht, V. Naschitz, B. Liu, S. Ghosh, N. Halperin, L. Halperin, D. Rozen, J. Power Sources 99 (2001) 7-14.
6. S. Licht, V. Naschitz, L. Lin, J. Chen, S. Ghosh, B. Liu, J. Power Sources 101/102 (2001) 167.
7. S. Licht, B. Wang, S. Ghosh, J. Li, R. Tel-Vered, Electrochem. Commun.2 (2000) 535.
8. Lj. N. Nikolić-Bujanović, M. Simičić, M. Čekerevac, Hem. Ind. 66 (4) (2012) 455 -460.
9. W.Yang, J. Wang, T. Pan, F. Cao, J. Zhang, Chu-nan Cao, Electrochim. Acta 49 (2004) 3455-3461.
10. J.M Schreyer, G.W.Thompson, L.T. Ockerman, J. Am. Chem. Soc., 22(1950)1426-1427.
11. S. Licht, X. Yu, In Ferrates; Sharma, V. Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 2008, pp. 2 - 51.
12. S. Wang, Z. Yang, D. Liu, S. Yi, W. Chi, Electrochem. Commun. 12 (2010) 367-370.
13. J. L. Coward, J. Biol. Phys.36 (2010) 405-425.
14. K. A. Walz, A. N. Suyama, W. E. Suyama, J. J. Sene, W. A. Zeltner, E. M. Armacanqui, A. J. Roszkowski, M. A. Anderson, Journal of Power Sources 134 (2004) 318-323.

THE INFLUENCE OF TETRAZOLE COMPOUNDS ON THE CORROSION BEHAVIOR OF COPPER IN 0.05 M NACL SOLUTION

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ABSTRACT

Inhibition of copper corrosion by 5-phenyl-1H-tetrazole and 1-phenyl-5-mercapto-1H-tetrazole in 0.05 M NaCl solution was examined. The methods used in the investigation were open circuit potential and potentiodynamic polarization measurements. The obtained results show that tetrazole compounds have good inhibitory properties in chloride medium. Kinetic parameters of copper corrosion were calculated from the potentiodynamic curves and were used to analyze the inhibitors adsorption mechanism on the metal surface. According to these results, 5-phenyl-1H-tetrazole and 1-phenyl-5-mercapto-1H-tetrazole act as mixed type inhibitor. The adsorption of investigated compounds obeys the Langmuir adsorption isotherm.

Key words: 5-phenyl-1H-tetrazole, 1-phenyl-5-mercapto-1H-tetrazole, corrosion inhibition, copper, sodium chloride.

INTRODUCTION

The use of copper in different industries is well known. Having that in mind, the corrosion process of copper and copper alloys is a major problem [1]. The most practical method to protect metals against corrosion and deterioration is application of inhibitors. Numerous inhibitors are investigated as potential corrosion inhibitors for copper and its alloys [2-4]. Organic compounds reduce the corrosion through adsorption processes on the metal surface and complex formation with metal ions [5]. The adsorption process is affected by the chemical structures of the inhibitors, the nature and charged surface of the metal. The corrosion rate will be decreased when the inhibitor molecules adsorbed and blocked active sites on the metal surface [6].

MATERIALS AND METHODS

The working electrode was made of copper, whereas the reference electrode was a saturated calomel electrode (SCE). The auxiliary electrode was made of platinum. The experiments were conducted in NaCl solution (0.05 M) and various concentrations of 5-phenyl-1H-tetrazole and 1-phenyl-5-mercapto-1H-tetrazole ($1 \cdot 10^{-5}$M - $5 \cdot 10^{-3}$M).

The electrochemical methods including open circuit potential measurements and potentiodynamic polarization measurements were used for this study. The open circuit potential was determined for 30 min upon which polarization curves were recorded. Linear voltammograms were recorded from the OCP to 0.5 V (vs SCE) in the anode direction and to -0.5 V (vs SCE) in the cathode direction. Scan rate was 1 mVs^{-1}.

RESULTS AND DISSCISION

The open circuit potential measurements of copper in 0.05M NaCl solution

The change of open circuit potential value (OCP) of copper is measured in 0.05M NaCl solution without and with the addition of different concentrations of tested inhibitors. The obtained curves are presented in Figures 1 and 2.

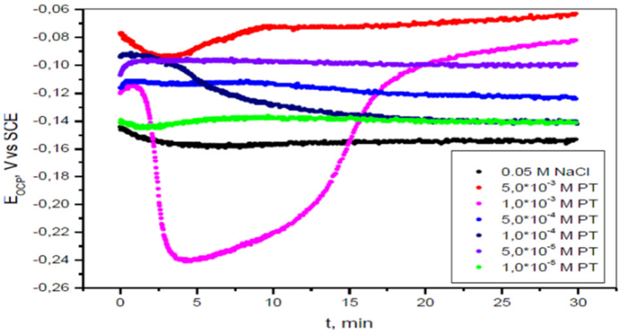


Figure 1. The open circuit potential values of copper in 0.05M NaCl without and with the addition of different concentrations of 5-phenyl-1H-tetrazole (PT)

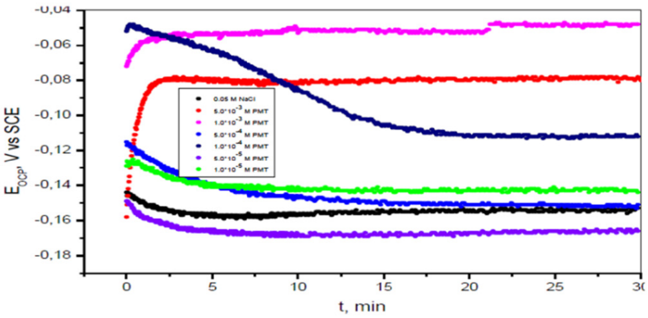


Figure 2. The open circuit potential values of copper in 0.05M NaCl without and with the addition of different concentrations of 1-phenyl-5-mercapto-1H-tetrazole (PMT)

According to the obtained results, it can be said that the OCP is shifted toward positive values in the presence of investigated compounds due to the adsorption of inhibitor molecules on the metal surface [7].

Potentiodynamic polarization measurements

Anodic dissolution of copper in chloride solution can be presented according to the reactions (1-3) [8, 9]. First comes to the formation of CuCl layer according to reaction (1). Further, CuCl layer has no ability to protect copper against corrosion and it transforms into $CuCl_2^-$ (reaction 2) [10].

$$Cu + Cl^- = CuCl_{ads} + e^- \tag{1}$$

$$CuCl_{ads} + Cl^- = CuCl_2^- \tag{2}$$

$$CuCl_2^- = Cu^{2+} + 2Cl^- + e^- \tag{3}$$

The cathodic reaction of copper in chloride solution can be presented as follows [11]:

$$4H^+ + O_2 + 4e^- = 2H_2O \tag{4}$$

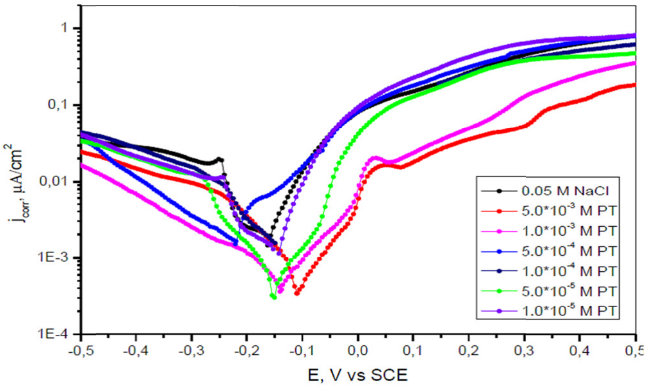


Figure 3. Polarization curves of copper in 0.05M NaCl solution without and with the addition of different concentration of 5-phenyl-1H-tetrazole (PT)

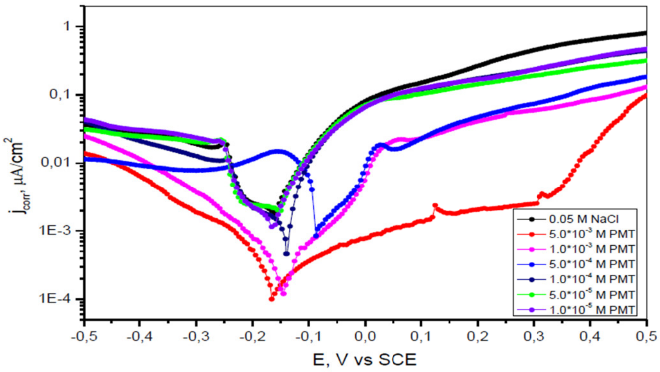


Figure 4. Polarization curves of copper in 0.05M NaCl solution without and with the addition of different concentration of 1-phenyl-5-mercapto-1H-tetrazole (PMT)

Potentiodynamic polarization curves of copper illustrated in Figures 3 and 4 imply that the addition of 1-phenyl-5-mercapto-1H-tetrazole and 5-phenyl-1H-tetrazole causes the decrease of corrosion current density. Also, the corrosion potential value becomes more positive with the 5-phenyl-1H-tetrazole concentration increase except for concentration of $5\cdot10^{-4}$M. In the presence of 1-phenyl-5-mercapto-1H-tetrazole there is no shift of the corrosion potential value. However, the addition of $5\cdot10^{-4}$M of 1-phenyl-5-mercapto-1H-tetrazole shifts the corrosion potential toward positive value. These findings lead to the conclusion that 1-phenyl-5-mercapto-1H-tetrazole and 5-phenyl-1H-tetrazole act as mixed type inhibitor. It is assumed that the compact film is formed on the copper surface and the chloride ions cannot react with metal [11, 12]. Corrosion parameters of copper oxidation in 0.05M NaCl solution in the absence and the presence of tetrazole inhibitors such as corrosion potential (E_{corr}), corrosion current density (j_{corr}) and inhibition efficiency (IE) are calculated and presented in Tables 1 and 2. The inhibition efficiency is obtained according to the equation (5):

$$\%IE = [(j_{corr} - j_{corr(inh)}) / j_{corr}]\cdot 100 \tag{5}$$

Where j_{corr} and $j_{corr(inh)}$ are corrosion current density recorded without and with inhibitor, respectively.

Table 1. Kinetic parameters of copper corrosion in 0.05M NaCl solution in the presence of various concentrations of 5-phenyl-1H-tetrazole

Inhibitor concentration, M	E_{corr}, V vs SCE	j_{corr}, μA/cm^2	IE, %
/	-0.160	0.0103	/
$1\cdot10^{-5}$	-0.140	0.0057	44.66
$5\cdot10^{-5}$	-0.151	0.0055	46.60
$1\cdot10^{-4}$	-0.120	0.0051	50.49
$5\cdot10^{-4}$	-0.225	0.0025	75.73
$1\cdot10^{-3}$	-0.140	0.000744	92.77
$5\cdot10^{-3}$	-0.107	0.000728	92.94

Table 2. Kinetic parameters of copper corrosion in 0.05M NaCl solution in the presence of various concentrations of 1-phenyl-5-mercapto-1H-tetrazole

Inhibitor concentration, M	E_{corr}, V vs SCE	j_{corr}, μA/cm^2	IE, %
/	-0.160	0.0103	/
$1\cdot10^{-5}$	-0.166	0.0038	63.10
$5\cdot10^{-5}$	-0.153	0.0034	66.99
$1\cdot10^{-4}$	-0.141	0.0026	74.76
$5\cdot10^{-4}$	-0.085	0.0022	78.64
$1\cdot10^{-3}$	-0.145	0.0010	92.29
$5\cdot10^{-3}$	-0.161	0.000303	97.05

By analyzing the obtained results, it can be seen that the increase of inhibitors concentration causes the increase of inhibition efficiency. Also, in the presence of 1-phenyl-5-mercapto-1H-tetrazole higher protection degree is achieved in comparison to the addition of 5-phenyl-1H-tetrazole.

The mechanism of corrosion inhibition in the presence of tetrazole compounds can be presented according to the following reactions [11]:

$$Cu + inh = Cu(inh)_{ads} = Cu^{n+} + ne^{-} + inh \tag{6}$$

$$inh_{aq} + nH_2O_{ads} = inh_{ads} + nH_2O_{aq} \tag{7}$$

Adsorption isotherm

In order to understand the corrosion inhibition mechanism, the adsorption of organic compounds on the copper surface is investigated. In this paper the Langmuir adsorption isotherm, presented as equation (8), is tested:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{8}$$

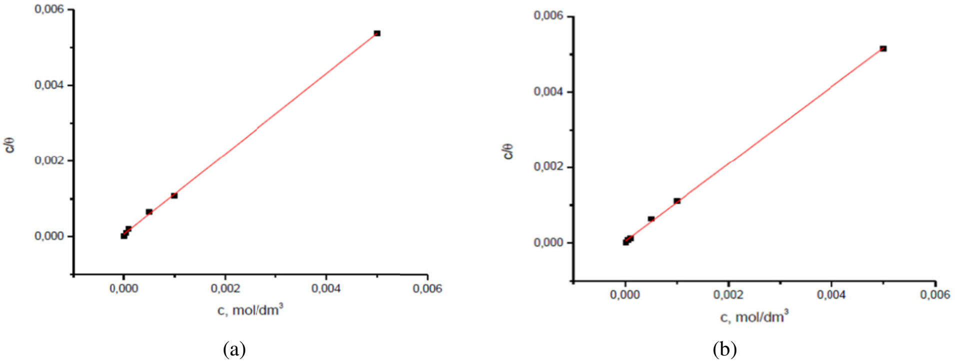
Where C_{inh} stands for concentration of inhibitor, K_{ads} is the adsorption constant and θ is the degree of surface coverage.

The Gibbs free energy of adsorption is calculated following the equation (9):

$$\Delta G_{ads} = -R \cdot T \cdot \ln(55.55 \cdot K_{ads}) \tag{9}$$

In which R is the universal gas constant, T is the thermodynamic temperature and 55.55 is the molar concentration of water.

Figure 5 shows a linear relationship of C/θ as a function of C and indicate that inhibitors adsorption follows the Langmuir adsorption isotherm. The calculated values of Gibbs free energies (ΔG_{ads}) are -33.43 kJ/mol and -33.87 kJ/mol for 5-phenyl-1H-tetrazole and 1-phenyl-5-mercapto-1H-tetrazole, respectively. The obtained values of ΔG_{ads} of tetrazoles indicate that the adsorption process includes physical and chemical type of interaction. Also, the negative sign implies the spontaneous adsorption mechanism on the copper surface [13, 14].



(a) (b)

Figure 5. The Langmuir adsorption isotherm in the presence of (a) PT and (b) PMT

CONCLUSION

In this paper the influence of tetrazole compounds on the corrosion behavior of copper in 0.05M NaCl solution is examined. The presence of the 5-phenyl-1H-tetrazole and 1-phenyl-5-mercapto-1H-tetrazole shifts the open circuit potential of copper toward positive values. According to the potentiodynamic polarization measurements, these compounds act as mixed type inhibitor. The mechanism of the corrosion inhibition process is based on the adsorption of inhibitors on the active corrosion sites. The adsorption of 5-phenyl-1H-tetrazole and 1-phenyl-5-mercapto-1H-tetrazole obeys Langmuir adsorption isotherm and calculated ΔG_{ads} indicates strong and spontaneous adsorption of the inhibitors on the copper surface.

Acknowledgement

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REFERENCES

1. Zhang, D, Xie B, Gao L, Cai Q, Joo H, Lee K, 2011, Intramolecular synergistic effect of glutamic acid, cysteine and glycine against copper corrosion in hydrochloric acid solution, Thin Solid Films 520, 356-361
2. Radovanovic, M, Antonijevic, M, 2016, Inhibition of brass corrosion by 2-Mercapto-1-methylimidazole in Weakly Alkaline Solution, Journal of Materials Engineering and Performance 25, 921-937
3. Petrovic Mihajlovic, M, Radovanovic, M, Tasic, Z, Antonijevic, M, 2017, Imidazole based compounds as copper corrosion inhibitors in seawater, Journal of Molecular Liquids 225, 127-136
4. Tasic, Z, Petrovic Mihajlovic, M, Antonijevic, M, 2016, The influence of chloride ions on the anti-corrosion ability of binary inhibitor system of 5-methyl-1H-benzotriazole and potassium sorbate in sulfuric acid solution, Journal of Molecular Liquids 222, 1-7
5. Milosev, I, Pavlinac J, Hodošček M, Lesar A, 2013, Amino acids as corrosion inhibitors for copper in acidic medium: Experimental and theoretical study, Journal of the Serbian Chemical Society 78, 2069-2086
6. Gece G, Bilgic S, 2010, A theoretical study on the inhibition efficiencies of some amino acids as corrosion inhibitors of nickel, Corrosion Science 52, 3435-3443
7. Sherif, E, Erasmus, R, Comins, J, 2010, In situ Raman spectroscopy and electrochemical techniques for studying corrosion and corrosion inhibition of iron in sodium chloride solutions, Electrochimica Acta 55, 3657-3665
8. Milić, S, Antonijević, M, 2009, Some aspects of copper corrosion in presence of benzotriazole and chloride ions, Corrosion Science 51, 28–34

9. Sherif, E, Erasmus, R, Comins, J, 2007, Effects of 3-amino-1,2,4-triazole on the inhibition of copper corrosion in acidic chloride solutions, Journal o Colloid and Interface Science 311, 144-151
10. Finsgar, M, Milosev, I, Pihlar, B, 2007, Inhibition of copper corrosion studied by electrochemical and EQCN techniques, Acta Chimica Slovenica 54, 591-597
11. Al-Mobarak, N, Khaled, K, Hamed, M, Abdel-Azim, K, 2011, Employing electrochemical frequency modulation for studying corrosion and corrosion inhibition of copper in sodium chloride solutions, Arabian Journal of Chemistry 4, 185-193
12. Quraishi, S, 2013, Electrochemical and theoretical investigation of triazole derivatives oncorrosion inhibition behavior of copper in hydrochloric acid medium, Corrosion Science 70, 161–169
13. Antonijević, M, Petrović, M, Radovanović, M, Radičević, M, 2007, Elektrohemijsko ponašanje bakra u rastvoru boraksa u prisustvu 1-fenil-5-merkapto tetrazola, Zaštita materijala 48, 29-37
14. Antonijević, M, Radovanović, M, Petrović, M, Ljubomirović, Z, 2008, Elektrohemijsko ponašanje mesinga u rastvoru boraksa u prisustvu 1-fenil-5-merkaptotetrazola, Zaštita materijala 49, 31-39

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HAZEL AS BIOMONITOR OF METAL POLLUTION ORIGINATING FROM COPPER SMELTER AND FLOTATION TAILING PONDS IN THE BOR AREA

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ABSTRACT

The biomonitoring ability of hazel (*Corylus* spp.) was assessed at three sampling sites in the vicinity of dominant sources of pollution and at the prevailing wind directions in comparison to the background site. The results indicated pollution of the soil with As, Cu, Fe, Pb and Zn as a result of emissions from the copper smelter and flotation tailing ponds. The content of Cu exceeded the remediation value at the sites UI, R1, R2. However, biological factors revealed low absorption of the elements from the soil to roots and leaves. In the terms of anthropogenic pollution, hazel acted as metal-excluding plant.

Key words: air pollution, copper smelter, flotation tailing ponds, hazel.

INTRODUCTION

Inorganic pollutants originating from point sources (e.g. industrial, urban and agricultural) are known to accumulate in the surface soil over time. However, soil cannot act as a final recipient because polluting substances are transferred by biogeochemical cycles to other systems. Plant response to deficiency or excess of elements in soil is not completely defined, because plants have developed mechanisms that have resulted in adaptation and tolerance to chemically imbalanced environments [1]. Metals and metalloids, originating from smelters of nonferrous metallurgy, mine tailings or overburden dumps, distributed by fugitive dust or waste waters, represent important environmental contaminants [2]. Suspended particles of the smallest diameter, rich in metals and metalloids, are known to behave as gases, because they could be dispersed at very long distances [3]. In order to obtain information about the pollution level, as well as to expand the knowledge on potential biomonitors of pollution, new plant species are investigated. Kabata–Pendias [4] suggested that complementary analysis of soil and plant material (under– and above–ground parts) should be always investigated in order to avoid incorrect interpretation of the results.

The data presented in the paper give the insight of behaviour of *Corylus* spp. (hazel) in the conditions of high environmental pollution through the analysis of content, accumulation and translocation of metals and metalloids.

MATERIAL AND METHODS

Exploitation and pyrometallurgical copper production are processes known for creating ecological problems near the involved facilities, which could be seen in the Bor area where the continuous mining–metallurgical operations have been carried out since the 1900's [2]. Three selected sites for the analysis (Figure 1a), were the sites with high level of atmospheric pollution and pronounced negative influence of dominant west winds which bring the polluting substances (Figure 1b) [5]. The site UI was located 0.5 km WSW from the copper smelter, in the urban part of the town of Bor. Besides emissions from the smelter, pollution at this site originated from the town heating plant (coal) and traffic, but in lower portion. The sites R1 and R2 represented rural settlements Oštrelj and Slatina, respectively. The site R1 was located 4.5 km ESE from the copper smelter and 1.7 km SSE from the flotation tailing ponds (F3 and F4) of the mine Veliki Krivelj, while the site R2 was located 6.5 km SE from the smelter and 6.0 km from the flotation ponds (F1 and F2) near the town of Bor (Figure 1a). At both of the R–sites, pollution also originated from the copper smelter and individual heating. The background site (B), located in the rural settlement Gornjane 17 km N from the smelter (not shown on the map), was the site without air pollution impact [6].

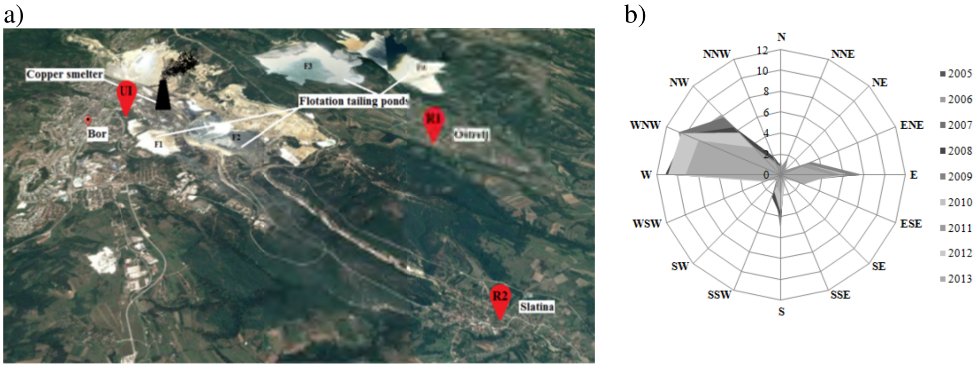


Figure 1. a) Sampling sites in the study area of Bor and the surroundings; b) A wind rose diagram for the period 2005–2013 (the annual frequency, %)

At each sampling site, soil and plant material of *Corylus* spp. (predominantly *C. avellana*, common hazel) was sampled from 3 to 5 individual trees to form composite samples which represented the sites UI, R1, R2 and B. The soil samples were taken from a depth of 20–30 cm, where the root samples were taken from, too. Leaves and catkins were sampled *in situ* from branches, sampled at the height of 1.5 m from the ground. In order to remove atmospheric depositions, leaves were washed with distilled water in a laboratory, unlike the branch and catkin samples [6]. Concentrations of As, Cr, Cu, Fe, Mn, Ni, Pb and Zn in all the samples were determined by ICP–AES in the Mining and Metallurgy Institute in Bor, after the digestion [7]. Prior to the chemical analysis, a standard procedure of the sample preparation, given in the literature, was employed, as well as determination of the soil pH [8] and the content of soil organic matter [9]. Biological factor analysis [6] included Biological Concentration Factor (BCF), Translocation Factor (TF), and Biological Accumulation Coefficient (BAC), which were calculated as following:

BCF=element conc. in root/element conc. in soil;
TF=element conc. in leaves/element conc. in root;
BAC=element conc. in leaves/element conc. in soil.

RESULTS AND DISCUSSION

In Table 1, the data for soil from the root zone of hazel are presented. The obtained concentrations from the polluted sites were compared to the corresponding concentrations from the background site (B), and with the defined concentrations from the current Regulation in Serbia concerning the soil pollution [10]. The concentrations of the studied elements at the sites UI, R1 and R2 were higher than the concentrations at the site B, except for Cr and partly Ni. The concentration differences among the sites were most evident in the case of Cu. The proposed limit values (LVs) [10] were exceeded for As (except at the site B), Cu (at all the sites), Ni (only at the site R1) and Zn (except at the site B). The defined remediation value (RV) [10] was exceeded only for Cu (except at the site B), while for As, the concentration at the site R2 was nearly the corresponding RV. According to the Regulation [10], the RVs indicated alarmingly polluted soil (in which the basic functions of soil are endangered or seriously impaired); and therefore remediation, recovery or other measures are required to be implemented. Regarding the soil pH, the results indicated rather neutral to alkaline reaction of the sampled soil [11], although the pH values of atmospheric depositions in the study area were in the range of 5.4–6.3 [12] at four measuring sites (*Hospital*, *Forest section*, *Institute, Oštrelj*) during the sampling year 2013. Soil organic matter (OM) showed medium content, from 6% to 20% [13], which could result in lower bioavailability of metals due to bonding to OM [4].

Table 1. Concentrations of the studied elements (mg kg^{-1}), pH value and content of organic matter (OM) in soil from four sampling sites

Site	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH (H_2O)	OM (%)
UI	**34.20**	24.69	**664.30**	41693.7	1056.2	13.84	45.70	**176.45**	7.52	7.24
R1	27.17	44.32	**450.83**	33800.0	1021.1	**35.58**	54.31	**276.73**	7.84	12.46
R2	**54.92**	32.27	**849.48**	42906.8	1087.5	17.0	68.50	**220.85**	7.50	10.95
B	8.40	66.11	**46.14**	29298.1	790.0	22.04	18.65	58.42	6.20	8.29
LV[a]	29	100	36	/	/	35	85	140	/	/
RV[b]	55	380	190	/	/	210	530	720	/	/

[a]LV–The limit value given by the Serbian Regulation [10]; [b]RV–The remediation value given by the Serbian Regulation [10]; Concentrations exceeding the LVs or RVs shown in bold; / Not defined.

Deficiency, normal and toxic element concentrations for plants have been proposed though the literature by many authors. However, the suggested concentrations are based on the wide ranges, which are sometimes overlapping, and often given for herbaceous plants and fodder, therefore not fully relevant for higher plants. The concentrations of the studied elements within the mentioned ranges are given in Table 2, while the obtained concentrations from the study area are shown in Figure 2.

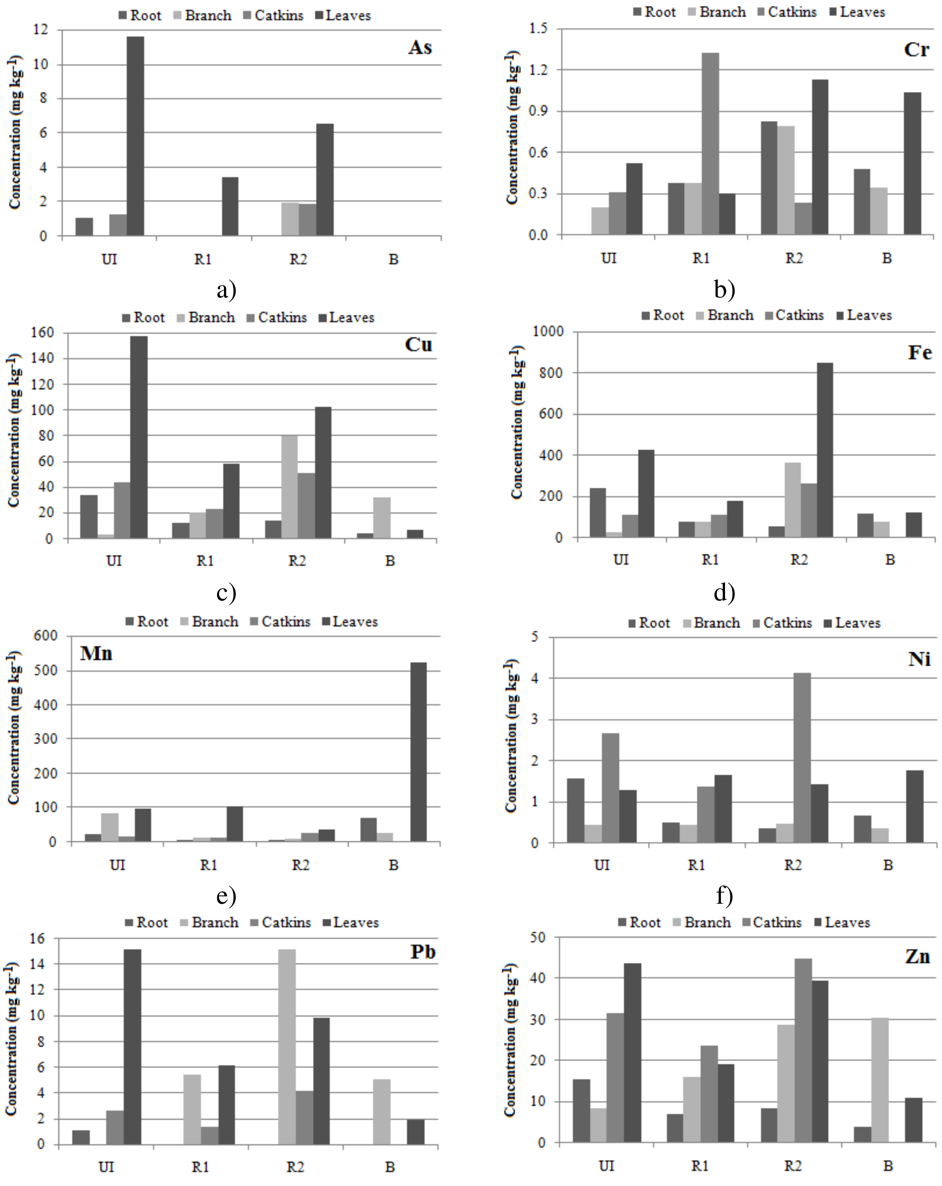
The arsenic content in hazel leaves was in toxic range at the sites UI, R1 and R2, while at the site B, As concentration was below the limit of determination in all the hazel parts (Fig. 2a). Chromium was present at all the sites and parts in ~~the~~ normal ranges, with the observed different Cr distribution in the parts regarding the sampling sites (Fig. 2b). The hazel parts contained copper in the range of deficit to toxic, although the normal and toxic ranges are overlapping (Table 2). Noticeably lower Cu concentrations were observed at the site B in all the parts, while the highest concentration (157.4 mg kg^{-1}) was detected in the leaves at the site UI. The general trend of increasing Cu concentrations was observed from roots toward hazel leaves (Fig. 2c). The normal and toxic ranges for Fe are also overlapping. However, except the Fe content in the leaves at the site R2, the rest of the hazel parts contained Fe in the normal range, with the observed slightly higher concentrations in the leaves (Fig. 2d). All the hazel parts contained Mn in the normal range, except the leaves sampled at the B site, where Mn content amounted to 523.3 mg kg^{-1} (Fig. 2e). The Ni content was also in the normal range (Fig. 2f) at all the sites, with higher accumulation in hazel catkins and leaves. The Pb content exceeded the normal range at the site UI in the leaf samples and at the site R2 in the root samples (Fig. 2g), but still below the toxic threshold. The content of Zn was from deficit to normal (Fig. 2h), with noticed accumulation in the aboveground hazel parts at the polluted sampling sites.

The literature data concerning sampling of hazel in the areas with pronounced emissions from the metallurgical operations are not available. Tomašević *et al.* [14] and Huseyinova *et al.* [15] presented data for traffic–related sites, which is not comparable with the presented data. However, Huseyinova *et al.* [15] reported contents of Cu, Fe and Zn from a non–polluted site in washed leaves of *C. avellana*: 9.1±1.7, 110.2±34.9 and 30.3±7.4 µg g^{-1}, respectively, which are very similar values to the obtained ones at the background site in this study.

Table 2. Three concentration ranges (mg kg^{-1}dw) in mature leaves of plants given by Kabata–Pendias [1]

Range	As	Cr	Cu	Fe*	Mn	Ni	Pb	Zn
Deficit	/	/	2–5	30–50	10–30	/	/	10–20
Normal	1–1.7	0.1–0.5	5–30	30–300	30–300	0.1–5.0	5–10	27–150
Toxic	5–20	5–30	20–100	400–1000	400–1000	10–100	30–300	100–400

/ Not given in the literature; *According to Pugh *et al.* [16].



a) b)

c) d)

e) f)

g) h)

Figure 2. Concentrations of studied elements (mg kg^{-1}dw) in hazel parts per sampling sites a) As; b) Cr; c) Cu; d) Fe; e) Mn; f) Ni; g) Pb; h) Zn (in the cases of missing bars, concentrations were below the limit of determination)

BIOLOGICAL FACTOR ANALYSIS

The values of the analysed biological factors are given in Table 3. According to the data, it can be concluded that the studied elements did not accumulate from soil into roots of hazel (BCF), probably because of low bioavailable concentrations due to the high pH value and/or high OM content in soil. The values of BCF did not vary per sampling sites, except for As and Ni where slightly higher accumulation was observed at the sites B and UI, respectively. Translocation of the studied elements from hazel roots to leaves (TF) occurred almost at all the sites (except for Cr and Ni in a few cases). It seems that all the accumulated quantity of the elements from soil into roots (although small according to BCFs), were translocated to leaves. However, a direct influence of soil element concentrations at their content in the leaves (BAC) was not observed. Except for Mn, for the rest of the studied elements, higher values of BAC were observed at the site UI in comparison to the site B, but still <1. According to Nagaraju and Karimulla [17], intensity of uptaking elements into leaves from soil was in the range of week (0.01–0.1) for Cr, Fe, Ni, to moderate (0.1–1) absorption for As, Cu, Pb and partly Mn and Zn.

Table 3. Biological factors for the studied elements

Factor	Site	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn
BCF	**UI**	0.030	0.037	0.051	0.006	0.023	0.112	0.024	0.088
	R1	<0.037	0.008	0.026	0.002	0.007	0.014	<0.018	0.026
	R2	<0.018	0.026	0.016	0.001	0.007	0.021	<0.015	0.038
	B	<0.119	0.007	0.096	0.004	0.088	0.030	<0.054	0.070
TF	**UI**	**11.233**	0.576	**4.613**	**1.772**	**3.945**	0.827	**13.911**	**2.826**
	R1	**>3.426**	0.804	**4.871**	**2.339**	**14.277**	**3.274**	**>6.134**	**2.721**
	R2	**>6.521**	**1.360**	**7.372**	**15.576**	**4.775**	**3.915**	**>9.853**	**4.661**
	B	/	**2.155**	**1.630**	**1.020**	**7.561**	**2.716**	**>1.919**	**2.722**
BAC	**UI**	0.339	0.021	0.237	0.010	0.092	0.093	0.333	0.249
	R1	0.126	0.007	0.129	0.005	0.102	0.046	0.113	0.070
	R2	0.119	0.035	0.121	0.020	0.033	0.084	0.144	0.179
	B	<0.119	0.016	0.156	0.004	0.662	0.081	0.103	0.191

BCF–Biological Concentration Factor; TF–Translocation Factor; BAC–Biological Accumulation Coefficient; The values >1 shown in bold; The values with > or < missing one of the concentrations replaced with the corresponding limit of determination; / No data since both concentrations were missing.

The obtained BACs could also be interpreted as proposed by Baker [18], in order to assess the biomonitoring ability of hazel. According to this author, the values BAC>1 indicate plants with the accumulating ability, BAC≈1 suggest the indication ability, while the values BAC<1 are related to exclusion abilities of the studied plants. Based on the classification, it seems that hazel acted as excluder plant in the polluted environment of Bor and the surroundings, since the linear dependence between soil and foliar concentrations of the analysed elements was not observed.

CONCLUSION

The biomonitoring ability of hazel was assessed at the sampling sites which were characterised with high level of air pollution due to the vicinity of dominant sources of pollution (copper smelter and flotation tailing ponds) and negative influence of the prevailing winds of west directions. The concentrations of the analysed elements showed clear influence of mining–metallurgical operations on the content of As, Cu, Fe, Pb and Zn in the soil, since the concentration were higher at the sites UI, R1 and R2 in comparison to the background site. The Cu content exceeded the proposed remediation value. The data presented in the paper also showed that hazel, as a widespread plant in the study area of Bor, showed different response to metal pollution, since the differences were observed between the polluted sampling sites and the background. The results of biological factors indicated that foliar concentrations of the elements were not the result of its soil content. In the study area, hazel behaved as metal excluding plant.

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REFERENCES

1. Kabata–Pendias A. (2011). Trace elements in soils and plants. CRC Press, Boca Raton.
2. Dimitrijević M., *et al*. (2009). Influence of pyrometallurgical copper production on the environment, J. Haz. Mat. (164) 892–899, Elsevier/Amsterdam.
3. [3] Barcan V. (2002). Nature and origin of multicomponent aerial emissions of the copper–nickel smelter complex, Environ. Internat. (28) 451–456, Elsevier/Amsterdam.
4. Kabata–Pendias A. (2004). Soil–plant transfer of trace elements–An Environmental Issue, Geoderma (122) 143–149, Elsevier/Amsterdam.
5. Serbula S.M., *et al*. (2013). Exceedance of air quality standards resulting from pyro–metallurgical production of copper: a case study, Bor (Eastern Serbia), Environ. Earth Sci. (68) 1989–1998, Springer/Berlin.
6. Radojevic A.A., *et al.* (2017). Metal/metalloid content in plant parts and soils of *Corylus* spp. influenced by mining–metallurgical production of copper, Environ Sci Pollut Research (*in press*) 1–15, Springer/Berlin.
7. U.S. EPA (1996). Acid Digestion of Sediments, Sludges, and Solids (3050B), Washington, USA.
8. ISO (2005). Soil Quality: Determination of pH, ISO 10390:2005, Geneva Switzerland.

9. Salehi M.H., *et al.* (2011). Refining Soil Organic Matter Determination by Loss-on-Ignition, Pedosphere (21)473–482, Elsevier/Amsterdam.
10. Regulation No. 88/10 (2010). The soil quality monitoring programme using indicators for assessing the risks from the soil degradation as well as the methodology for working out the remediation programme, "The Official Gazette of the Republic of Serbia".
11. Sparks D.L. (2003). Environmental soil chemistry, 2nd ed., Academic Press, San Diego.
12. MMI (2013). The annual report on the air quality control in Bor; The Mining and Metallurgy Institute in Bor, Serbia.
13. ISO 14688–2, Geotechnical investigation and testing–Identification and classification of soil, Part 2: Principles for a classification, Geneva Switzerland.
14. Tomašević M., *et al.* (2008). Contribution to biomonitoring of some trace metals by deciduous tree leaves in urban areas. Environ. Monit. Assess. (137) 393–401, Springer/Berlin.
15. Huseyinova R., *et al.* (2009). Sulphur and some heavy metal contents in foliage of Corylus avellana and some roadside native plants in Ordu Province, Turkey. Ekoloji (18) 10–16, Index Copernicus/Izmir.
16. Pugh R.E., *et al.* (2002). Heavy Metal (Pb, Zn, Cd, Fe, and Cu) Contents of Plant Foliage Near the Anvil Range Lead/Zinc Mine, Faro, Yukon Territory, Ecotox. Environ Safety (52) 273–279, Elsevier/Amsterdam.
17. Nagaraju A. and Karimulla S. (2002). Accumulation of elements in plants and soils in and around Nellore mica Belt, Andhra Pradesh, India–a biogeochemical study, Environ. Geo. (41) 852–860, Springer/Berlin.
18. Baker A.J.M. (1981). Accumulators and Excluders: Strategies in the Response of Plants to Heavy Metals, J. Plant Nutrit. (3) 643–654, Taylor&Francis Online/Abingdon.

INDUSTRIAL POLLUTION OF THE DANUBE AT THE SITE OF SMEDEREVO

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ABSTRACT

The aim of this paper was to present the state of the water quality of the Danube River according to the content of nutrients at the location of Smederevo in Serbia. Monthly fluctuations of total of six water quality parameters were observed for the year of 2013. Afterwards, calculated values were compared with the limit values prescribed by the National Regulation. It was determined that according to indicators of nutrient content in the water the Danube water quality did not meet the requirements of the first class of water quality at this very location. The results of this analysis indicate that the water pollution could be the result of bad industrial conditions and operating mode in Smederevo municipality.

INTRODUCTION

Aquatic ecosystems contain significant amounts of organic and inorganic nitrogen and phosphorus compounds. Nutrients such as nitrogen and phosphorus, if present in increased concentrations in the aquatic ecosystem stimulate the growth of algae and other photosynthetic organisms, which affects acceleration of eutrophication (Figure 1). Natural eutrophication is a process in which the lakes by "aging" are becoming more productive, but human beings with its different activities greatly affect the acceleration of the process of eutrophication [1]. Increased concentrations of nutrients cause excessive algae growth and reduce the concentration of oxygen dissolved in the water, which has a negative impact on wildlife aquatic ecosystems [2]. In addition eutrophic waters increase water treatment costs if they are used as a source of water supply.

Figure 1. The growth changes in algae population [3]

The main sources of nitrogen and phosphorus compounds are the agricultural areas, as well as the discharge of untreated or insufficiently treated water used. In order to prevent the negative effect of nitrogen on aquatic ecosystems, the water is purified before being discharged necessary to the extent required.

The industrial zone of Smederevo includes two large areas, ie the areas that are characterized by the greatest threats to the environment [4]. Industrial Zone of Smedereo covers an area of 260 hectares in which the greatest part of the industry of Smederevo (metal working industry and mechanical engineering) is located. Waste water originate from the 23 companies that get into the Danube through the drainage network and open drainage network in Godominska field through the pumping station " Smederevo ". The largest part of the waste water comes from three companies: " Milan Blagojević ", " Fagram " and " Simaks " [5].

METHODOLOGY

The analysis included six indicators of nutrient content in the water: total nitrogen (N), nitrite (NO_2-N), nitrate (NO_3-N), orthophosphate (PH_4-P), ammonium (NH_4-N) and total phosphorous (P).Water quality monitoring data was collected during the time period from January to December 2013 by the Republic Hydro-meteorological Service of Serbia (RHMS). Yearly averaged values were calculated for the purpose of the investigation. Limit values of pollutants in surface waters according to Serbian legislation [6] were used to determine the class of the Danube water quality at selected location.

RESULTS AND DISCUSSION

Values of the six observed parameters measured on monthly basis were averaged in order to obtain average yearly values to be compared with the prescribed, limit values (Table 1). It can be seen that only nitrates are within the class I of water quality, while all the other parameters put the water quality of the Danube into lower classes than preferred (class II and III).

Table 1. Averaged values of the observed parameters along with prescribed values

Nutrients	Units	Calculated values	I class	II class	III class	IV class	V class
N	mg/l	1,73	1	**2**	8	15	>15
NO_2-N	mg/l	0,02	0,01	**0,03**	0,12	0,3	>0,3
NO_3-N	mg/l	0,74	**1**	**1**	6	15	>15
NH_4-N	mg/l	0,15	0,10	0,10	**0,6**	1,5	>1,5
P	mg/l	0,08	0,05	0,05	**0,4**	1	>1
PH_4-P	mg/l	0,04	0,02	0,02	**0,2**	0,5	>0,5

Graphical display of variations in levels of nutrients during the year, on a monthly basis, is presented in Figure 1. It can be concluded that the increase in nutrients values took place in the spring (in April) and autumn (starting from September till the early December), which could be related to the temperature regime of the water and the climate changes of the environment.

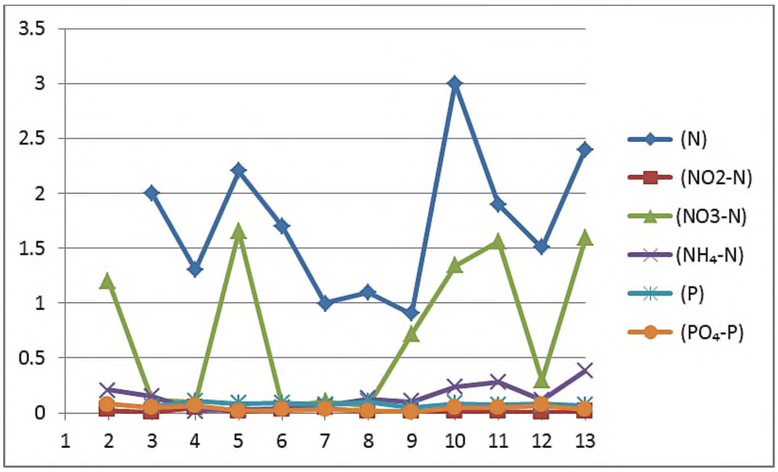

Figure 1. Monthly fluctuations in the observed values of nutrients in the water

Still, industry of Smederevo is supplied with water from the Danube River and the main receivers of wastewater are the Jezava, the Ralja, the Konjska reka, the

Vučačka stream and a number of drainage channels. In the industrial area there are companies of various activities, so the affected Danube water is used to perform various technological processes. As a result of such usage, water polluted with different physico-chemical and microbiological characteristics emerge. Many companies have built systems for treatment of waste water prior to its discharge into the Danube, but they are often unable to function or not functioning efficiently enough. When industrial facilities are operating at full capacity, the total amount of waste water that enters into the Danube is more than 60 000 m^3 per month. Half of the amount is generated by the three companies - "Milan Blagojević", "Fagram" and "Simaks". They gather exploited water in a common collector, with the faeces, sanitary and storm water, from which the water is further discharged into the Danube, using only their own pumps [5]. The results of this analysis indicate that the water pollution could be the result of such operating mode and industrial conditions in Smederevo municipality.

CONCLUSION

The analysis shows that the Danube water quality at the site of Smederevo is with the increased concentrations of nutrients. Other studies on this location have also shown that the most polluted surface water registered results in high concentrations of ammonium, nitrate, phosphate and heavy metal ions. Aiming at better monitoring of the quality of wastewater and its treatment technology, it is necessary to perform regular control of wastewaters of all companies registered in a register of polluters, following the dynamics of the harmonized regulations.

REFERENCES

1. Carpenter, S. R. et al. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8, 559-568
2. Dodds, W. K. et al. (2009). Eutrophication of U.S. freshwaters: analysis of potential economic damages. Environmental Science and Technology 43, 12-19
3. Web source: http://www.bio.bg.ac.rs/materijali_predmeta/07-eutrofikacija.pdf
4. Milanović, A. Kovacevic Majkić, J., Milivojević, M. (2010). Analysis of water quality of the Danube in Serbia - problems of pollution and protection. Bulletin of the Serbian Geographical Society, 90 (2), 47-68.
5. Gavrilović, Lj. Miladinović S. (2009). Pollution watercourses in the municipality of Smederevo and their protection, Proceedings PMF-Geographical Institute, Belgrade, 57, 19-34.
6. Regulation on limit values of pollutants in surface and ground waters and sediments, and deadlines for their achievement (Official Gazette no. 50/2012).

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IN SITU SYNTHESIS OF BIOCOMPATIBLE COMPOSITE LAYER OF HYDROXYAPATITE/PASSIVE OXIDE SURFACES ON THE MODIFIED TITANIUM

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ABSTRACT

Hydroxyapatite (HAp) is the most suitable biocompatible material for bone implant coatings. However, its brittleness is a major obstacle, and that is why, recently, research focused on creating composites. In this study, a novel in situ synthesis of HAp coating on titanium was presented. HAp was anaphoretically deposited from alkaline-ethanol suspension in one step process. Morphology of the coating was investigated by optical microscopy, while deposited HAp was characterized using ATR-FTIR. It was concluded that HAp has excellent coverage of the surface without delamination. The obtained coating can be good material for bone implants due to solving HAp brittleness.

Key words: hydroxyapatite, anaphoretic deposition, titanium, FTIR.

INTRODUCTION

In recent years, new materials for use in orthopedic surgery have been the subject of extensive research. The main challenges of biological implants have an appropriate hardness, adhesion, biocompatibility and corrosion resistance. Titanium is one of a small number of biocompatible metals which has been successfully used as dental and medical implants, since it has advantageous properties such as strength, toughness, density, low Young's modulus, corrosion resistance and biocompatibility, which makes it suitable material for biomedical applications [1-6]. However, it was shown that titanium is not an ideal replacement for bone tissue due to differences in its physical and chemical characteristics in relation to the bone, which is reflected in poor osteoconductivity and osteoinductivity [7, 8]. On the other hand, the titanium can cause an adverse reaction of the body upon its implantation [9]. Although little of this problem is reported in the literature, there are isolated cases and studies to prove it.

In order to increase osteointegration and improve regeneration of the bone tissue on the implant, modification of titanium surface is required with a biologically active material. The most commonly used biocompatible material is a hydroxyapatite

(HAp, $Ca_{10}(PO_4)_6(OH)_2$) [10]. Hydroxyapatite has the chemical structure that resembles bone mineral composition with similar release of Ca^{2+} и PO_4^{3-} ions and it can be used during the formation of new bone formation [11-13]. HAp has porous structure and due to its bioactivity HAp leads to its partial resorption and replacement of natural bone cells [14]. It has the possibility of creating a strong chemical bonds with bones.

Electrophoretic deposition (EPD) is another method of surface modification that is used for improving the bioactivity of the surfaces by deposition of calcium phosphate (CaP) particles on TiO_2 electrode under high voltage [15-17]. The advantages of this method are rapid formation of the coating, simple instrumentation, deposition of very pure stoichiometric coatings on complex surfaces. However, the EPD technique does not provide good adhesion of the coating to the substrate. Due to major differences between the properties of the bioactive material and the metal substrate, adhesion of the coating to the substrate remains a major problem. During review of the literature it has been observed that most of the works dealing with a modification of the coating and the surface of the substrate without adhesion tests between them [7, 10, 17-19], nor adequate adhesion testing were performed which include mechanical testing [20]. The problem of poor adhesion of the coating appears in the form of delamination, poor mechanical properties and poor connections between the ceramic and metal. A potential solution to this problem is seen in the methods of surface modification of the substrate and/or HAp coatings in order to improve adhesion. Papers that have dealt with the adhesion of the coatings and substrate modifications [21-23] did not suggest a process which would, in the same time, modify the coating and substrate, regardless of the relatively positive obtained results of adhesion.

Anodizing the substrate surface has proven to be a promising method of modifying metals. One of the most commonly used method is the anodization of surface with simultaneous treatment in an acidic environment, and a bioactive electrodeposition of HAp coating. On the other hand, it was shown that pre-treatment of alkali nanotubular titanium oxides (ATi) accelerates the formation of HAp, having the characteristics and structure as the bone tissue [24]. Nanostructured HAp is formed on the pretreated and ATi ATi (P-ATi), in contrast with conventional Ti [24].

The aim of the work was novel process of *in situ* synthesis and characterization of anaphoretic hydroxyapatite coatings on modified titanium surfaces by anodization process.

EXPERIMENTAL

A chemical precipitation method was used to prepare hydroxyapatite powder by the reaction of calcium oxide (obtained by calcination of $CaCO_3$ for 5 h at 1000 °C in air) and phosphoric acid. A stoichiometric amount of the resulting calcium oxide was mixed and stirred in distilled water for 10 min and phosphoric acid was added dropwise to the suspension in order to obtain hydroxyapatite powder, $Ca_{10}(PO_4)_6(OH)_2$. When all the necessary quantity of phosphoric acid was introduced, the pH reached a value of 7.4–7.6. The obtained suspension was preheated to 94 ± 1 °C for 30 min and stirred for another half an hour. After sedimentation, the upper clear solution layer was decanted. The suspension was then spray-dried at 120 ± 5 °C into granulated powder [25]. HAp powder was then suspended in a solution containing 5 wt.% of NaOH with 50% of C_2H_5OH.

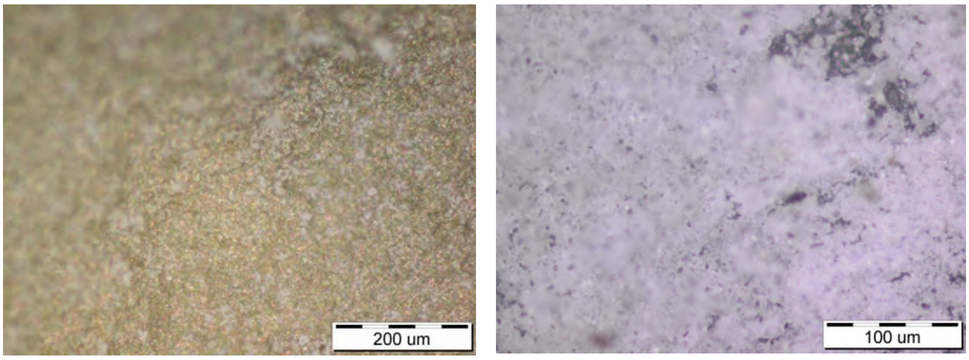
Electrochemical measurements were performed in a two-electrode cell. For this purpose, an electrochemical work station (Hewlett Packard HP6024A) having potentiostat/galvanostat provided with corrosion and physical electrochemistry software and a desktop computer (HP) was used. A platinum wire was used as counter electrode. The working electrode geometric area exposed to electrolyte was 0.39 cm^2. The cell was filled with HAp suspension and purged with N_2 for 30 min prior to electrochemical measurements.

Morphology of the obtained HAp coatings was determined by optical microscope Olympus BX41.

Fourier transform infrared spectroscopy (FTIR) was recorded on anodized titanium and on anaphoretic deposited HAp coating composite. Michelson MB Series Bomen FTIR was used (Hartmann Braun), scanning from 400 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

In order to obtain *in situ* HAp coating and to compare it with pure Ti after anodzation, two sets of experiments were performed, i.e. pure titanium anodization and anaphoretic HAp coating deposition from alkaline solution. For HAp to be anaphoreticaly deposited, it needs to be in a form of suspension with negatively charged micelle. Pure ethanol in 5 % NaOH was proven to be excellent solution of choice for this task, making HAp suspension stable for a long period of time. Both anodization and anaphoretic deposition were performed from 50-70 V at 0.5 mA in galvanostatic regime for 5 min. Obtained anodized titanium surface and deposited HAp coating are shown in Figure 1.



(a) (b)

Figure 1. Optical images of (a) anodized titanium and (b) HAp coating on titanium

It can be seen that HAp has excellent coverage of the surface with a firm deposite that is not delaminating. The obtained coating can be good material for bone implants due to solving HAp brittleness. Further evidence of presence of HAp coating on titanium, and hence its functional groups is characterized by ATR-FTIR spectrum which is shown in Figure 2.

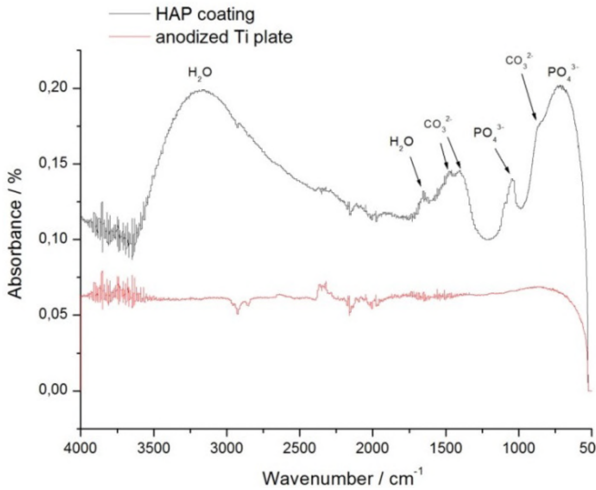


Figure 2. ATR-FTIR spectrum of anodized titanium (bottom red line) and HAp coating (top black line)

The spectra display typical PO_4^{3-} characteristic bands of hydroxyapatite coating. Two absorption bands were clearly distinguished at the following wave numbers 1041 and around 718 cm^{-1} in the ν_3 and ν_1 phosphate mode region. Additional weak bands at 872, 1402, and 1476 cm^{-1} are assigned to carbonate species (CO_3^{2-}) in the apatite lattice [26]. These peaks in the FTIR spectrum can be attributed to the reaction between CaO and CO_2 from the atmosphere. In the FTIR spectrum of HAp coating (Figure 2), the wide band at 3170 cm^{-1} is attributed to the OH stretching of H_2O molecules. The band at cca. 1650 cm^{-1} is from water (bending modes). The observed functional groups and their corresponding assignments are presented in Table 1.

CONCLUSIONS

Nano-hydroxyapatite coating has been successfully synthesized by novel *in situ* method of anaphoretic deposition on titanium substrate. The formation of hydroxyapatite coating was confirmed by optical microscopy and Attenuated Total Reflection Fourier transform infrared spectroscopy (ATR-FTIR). It can be concluded that with good preparation and proper choice of suspension medium leading to stable negative micelle HAp obtains excellent coverage of the surface with a firm deposite that is not delaminating. This coating has good properties to be used as a material for bone implants.

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REFERENCES

1. Ahmadi, S.; Mohammadi, I.; Sadrnezhaad, S. K., Hydroxyapatite based and anodic Titania nanotube biocomposite coatings: Fabrication, characterization and electrochemical behavior. *Surface and Coatings Technology*, 287, 67-75, 2016.
2. Liu, X.; Chu, P. K.; Ding, C., Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Materials Science and Engineering: R: Reports*, 47, (3–4), 49-121, 2004.
3. Ahmadi, S.; Sadrnezhaad, S. K., A novel method for production of foamy core@compact shell Ti6Al4V bone-like composite. *Journal of Alloys and Compounds*, 656, 416-422, 2016.
4. Geetha, M.; Singh, A. K.; Asokamani, R.; Gogia, A. K., Ti based biomaterials, the ultimate choice for orthopaedic implants – A review. *Progress in Materials Science*, 54, (3), 397-425, 2009.
5. Dezfuli, S. N.; Sadrnezhaad, S. K.; Shokrgozar, M. A.; Bonakdar, S., Fabrication of biocompatible titanium scaffolds using space holder technique. *Journal of Materials Science: Materials in Medicine*, 23, (10), 2483-2488, 2012.
6. Long, M.; Rack, H. J., Titanium alloys in total joint replacement—a materials science perspective. *Biomaterials*, 19, (18), 1621-1639, 1998.
7. Han, C.; Wang, Q.; Song, B.; Li, W.; Wei, Q.; Wen, S.; Liu, J.; Shi, Y., Microstructure and property evolutions of titanium/nano-hydroxyapatite composites in-situ prepared by selective laser melting. *Journal of the Mechanical Behavior of Biomedical Materials*, 71, 85-94, 2017.
8. Hamada, K.; Kon, M.; Hanawa, T.; Yokoyama, K. i.; Miyamoto, Y.; Asaoka, K., Hydrothermal modification of titanium surface in calcium solutions. *Biomaterials*, 23, (10), 2265-2272, 2002.
9. Osman, R.; Swain, M., A Critical Review of Dental Implant Materials with an Emphasis on Titanium versus Zirconia. *Materials*, 8, (3), 932, 2015.
10. Niespodziana, K.; Jurczyk, K.; Jakubowicz, J.; Jurczyk, M., Fabrication and properties of titanium–hydroxyapatite nanocomposites. *Materials Chemistry and Physics*, 123, (1), 160-165, 2010.
11. Shen, S.; Cai, S.; Li, Y.; Ling, R.; Zhang, F.; Xu, G.; Wang, F., Microwave aqueous synthesis of hydroxyapatite bilayer coating on magnesium alloy for orthopedic application. *Chemical Engineering Journal*, 309, 278-287, 2017.
12. Shadanbaz, S.; Dias, G. J., Calcium phosphate coatings on magnesium alloys for biomedical applications: A review. *Acta Biomaterialia*, 8, (1), 20-30, 2012.
13. Abdal-hay, A.; Vanegas, P.; Hamdy, A. S.; Engel, F. B.; Lim, J. H., Preparation and characterization of vertically arrayed hydroxyapatite nanoplates on electrospun nanofibers for bone tissue engineering. *Chemical Engineering Journal*, 254, 612-622, 2014.
14. Williams, D. F., Tissue-biomaterial interactions. *Journal of Materials Science*, 22, (10), 3421-3445, 1987.

15. Albayrak, O.; El-Atwani, O.; Altintas, S., Hydroxyapatite coating on titanium substrate by electrophoretic deposition method: Effects of titanium dioxide inner layer on adhesion strength and hydroxyapatite decomposition. *Surface and Coatings Technology*, 202, (11), 2482-2487, 2008.
16. Biest, O. O. V. d.; Vandeperre, L. J., Electrophoretic Deposition of Materials. *Annual Review of Materials Science*, 29, (1), 327-352, 1999.
17. Ulasevich, S. A.; Kulak, A. I.; Poznyak, S. K.; Karpushenkov, S. A.; Lisenkov, A. D.; Skorb, E. V., Deposition of hydroxyapatite-incorporated TiO2 coating on titanium using plasma electrolytic oxidation coupled with electrophoretic deposition. *RSC Advances*, 6, (67), 62540-62544, 2016.
18. Wen, H. B.; de Wijn, J. R.; Cui, F. Z.; de Groot, K., Preparation of calcium phosphate coatings on titanium implant materials by simple chemistry. *Journal of Biomedical Materials Research*, 41, (2), 227-236, 1998.
19. Wang, H.; Eliaz, N.; Xiang, Z.; Hsu, H.-P.; Spector, M.; Hobbs, L. W., Early bone apposition in vivo on plasma-sprayed and electrochemically deposited hydroxyapatite coatings on titanium alloy. *Biomaterials*, 27, (23), 4192-4203, 2006.
20. Eliaz, N.; Shmueli, S.; Shur, I.; Benayahu, D.; Aronov, D.; Rosenman, G., The effect of surface treatment on the surface texture and contact angle of electrochemically deposited hydroxyapatite coating and on its interaction with bone-forming cells. *Acta Biomaterialia*, 5, (8), 3178-3191, 2009.
21. Mostafa, N. Y.; Kamel, M. M., Enhancement of adhesion bonding between titanium metal and electrodeposited calcium phosphate. *Surface Engineering and Applied Electrochemistry*, 52, (6), 520-523, 2016.
22. Hieda, J.; Niinomi, M.; Nakai, M.; Cho, K.; Matsubara, A., Evaluation of Adhesion of Hydroxyapatite Films Fabricated on Biomedical β-Type Titanium Alloy after Immersion in Ringer's Solution. *Mater. Trans.*, 56, (10), 1703-1710, 2015.
23. Eliaz, N.; Ritman-Hertz, O.; Aronov, D.; Weinberg, E.; Shenhar, Y.; Rosenman, G.; Weinreb, M.; Ron, E., The effect of surface treatments on the adhesion of electrochemically deposited hydroxyapatite coating to titanium and on its interaction with cells and bacteria. *Journal of Materials Science: Materials in Medicine*, 22, (7), 1741-1752, 2011.
24. Parcharoen, Y.; Termsuksawad, P.; Sirivisoot, S., Improved Bonding Strength of Hydroxyapatite on Titanium Dioxide Nanotube Arrays following Alkaline Pretreatment for Orthopedic Implants. *Journal of Nanomaterials*, 2016, 13, 2016.
25. Eraković, S.; Janković, A.; Veljović, D.; Palcevskis, E.; Mitrić, M.; Stevanović, T.; Janaćković, D.; Mišković-Stanković, V., Corrosion Stability and Bioactivity in Simulated Body Fluid of Silver/Hydroxyapatite and Silver/Hydroxyapatite/Lignin Coatings on Titanium Obtained by Electrophoretic Deposition. *The Journal of Physical Chemistry B*, 117, (6), 1633-1643, 2013.
26. Mirzaee, M.; Vaezi, M.; Palizdar, Y., Synthesis and characterization of silver doped hydroxyapatite nanocomposite coatings and evaluation of their antibacterial and corrosion resistance properties in simulated body fluid. *Materials Science and Engineering: C*, 69, 675-684, 2016.

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ELEMENT TRANSPORT IN *RUMEX OLYMPICUS* BOISS. FROM ABANDONED TUNGSTEN MINE WORK

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ABSTRACT

Plant species may show tolerance to increased element content in the environment and safely accumulate them. The genus *Rumex* comprises around 200 species which are widely used as medicinal herbs and foods globally [1]. Some species of this genus were mentioned as wild edible green vegetables [2].We evaluated the W, Cd, Cu, etc. contents of the leaves of *Rumex olympicus* which was collected from abandoned tungsten mine in the respect of health risk evaluation. This species is endemic and the dominant pioneer species on wet sites of Uludağ Mountain-Turkey.

Key words: Sorrel (*Rumex* spp.), risk assessment, abandoned mine work, ICP-MS.

INTRODUCTION

Some heavy metals/metalloids such as Fe, Mn, Zn, Ni, Mo, Co etc. are accepted as essential elements for plants because of their different roles in plant metabolism [3]. They can be taken up alongside nutrients with water and incorporated into plant tissues under natural conditions. Although many of metals are necessesary for plant metabolism, they can affect plants via different ways if they present at non-physiological concentrations. Imbalances in ion homeostasis of plants can lead to variations in many metabolic processes such as adaptation and defence mechanism. Plants can develop different strategies which are containing the avoidance of exposure, minimizing their uptake, and intracellular sequestering to mitigate the harmfull effects of heavy metal ions [4]. Many natural plants can survive, grow and reproduce not only natural heavy metal-rich but also heavy metal polluted soils as a result of anthropogenic activities such as mining, agricultural and industrial parctices. Natural plants spread heavy metal-rich soils can be classified as excluders, indicators and accumulators depending on their behaviour to elevated concentrations of heavy metals in surrounding soils [5]. Excluders plants have capable to tolerate excesses heavy metal concentrations in the environment by restricting the entrance of them and they can reduce the harmful effects by minimizing the transportation to the leaves [6]. Indicators are plant species which can tolerate heavy metals by reflecting their concentrations in the surrounding environment. The third group of plants which are called accumulators have capability to safely accumulate heavy metals in the aboveground tissues where the concentration is higher than in the soil [5]. The sub-group of these plants which is called hyperaccumulator are capable to accumulate metals in shoots in very large amounts [7]. Accumulator and hyperaccumulator plant species are the main tools of phytoremediation that is a relatively new clean-up technique, Therefore, the recent studies are focused on the determinig the plant species which can be considered as candidate for phytoremediation. The genus *Rumex* (sorrel) belonging to Polygonaceae family consist of around 200 species on the whole world [1] and many of them have traditional uses in the view of ethnobotanical and ethnopharmacological. For example, it was reported that *R. acetosa*, *R. acetosella*, *R. abyssinicus*, *R. crispus*, *R. sanguineus*, *R. tuberosus R. thyrsiflorus* and *R. vesicarius* serve as food via their leaves [8]. Similarly, it was reported that the seeds of *R. patienta* are used as medicine against to inflammation, diabetes, hyperlipidaemia, digestive disorders and skin disease [9, 10]. Morever, some *Rumex* species such as *R. obtusifolius* and *R. patientia* were investigated in regarding to their interactions with the heavy metals and heavy metal accumulation capacity [11, 12]). The other *Rumex* species, *R. olympicus* Boiss. is endemic to Uludağ Mountain (Bursa, Turkey) and is the dominant species of ruderal formation degraded wet sites [13, 14]. It also spread on degraded areas around the abandoned tungsten mine work. Although there have been a few studies related to this species like a study which reports *R. olympicus* as a new host for the larvae of *Lycaena dispar* [15], the studies on the ecological role of this species are restricted. In this study, we aimed to understand whether the elemental transportation of *Rumex olympicus* is changed by tungsten mine work activities and whether this species have a role in the clean-up of heavy metal contaminated soils through the accumulation. For this reason, we analyzed the elemental composition (W, Fe, Mo, Zn, Cu, Cd, Pb, Mn, B, Co, Cr, Bi) in the leaves of *R. olympicus* and it's surrounding soils.

MATERIAL AND METHOD

Material

R. olympicus Boiss. is an erect perennial. Stems tall, basal leaves oblong-ovate, somewhat acute; secondary veins in the middle part of the leaf forming an angle of 60-90° with the main vein. Lower lomeruli rather distant, the upper contiguous. Pedicels filiform, articulated below the middle. Inner perianth segments enlarged in fruit, cordate, c. 5 x 6 mm, only one tuberculate. Nut brown. It is very similar to *R. patientia.*

Sample sites and sampling

The study was performed on three samples sites (I, II, III) which were selected around the abandoned Etibank tungsten mine work from Uludağ Mountain (Bursa-Turkey). Sites I and II were selected approximately 500 m from the mine work by assuming they were unpolluted. On the other hand, site III was selected from the waste removal pool (WRP) and accepted as polluted site. After, leaf samples were taken from three individual plants (n=3), they were washed; and then dried in an oven until their weights became constant.The soils of each individual plants were taken from 0- to 15 cm depth and they were air dried in laboratory conditions. The leaf and soil samples which were homogenized by grinding with a mortar and pestle were stored in clear paper bags for element analyses.

Analysis

Elan 9000 inductively coupled plasma–mass spectrometry (ICP-MS) (PerkinElmer SCIEX, Shelton, CT, USA) was used to determine the content of W, Fe, Mo, Zn, Cu, Cd, Pb, Mn, B, Co, Cr, and Bi in soils and the plant tissues (leaves). A Perkin–Elmer Ryton cross-flow nebulizer, a Scott-type double-pass spray chamber, a standard glass torch, nickel sampler and skimmer cones (i.d.:1.1 and 0.9 mm, respectively) were the components of the ICP-MS equipment. Additionally, the optimum instrument conditions were as follows: RF power: 1000 W; plasma argon flow rate: 17.0 L min-1; nebulizer gas flow rate: 0.85 L min-1; sample uptake rate: 1.5 mL min-1; dwell time: 50 ms; scanning mode: peak hopping; and detector mode: dual. The classical open wet digestion procedure was applied to the samples (300-500 mg) with 3 mL HNO3 and 1 mL H2O2 in a borosilicate glass vessel. A single-element standard solution of tungsten at a concentration of 1000 lg mL-1 (Perkin Elmer) and a multielement standard solution of 30 elements (Merck 110580) were used to prepare working solutions for external calibration. Calibration curves were constructed with seven points (5.6–3000 lg L-1 for W) [16]. The differences among the sampling sites regarding the elemental content of plants and soil samples were tested using a one-way ANOVA. We used Tukey's HSD test to determine the differences among sample sites. All tests were analyzed using a significance level of 0.05. Statistical analyses were carried out using the Statistica Ver 6.0 (Stat Soft Inc. 1984–1995) program.

RESULTS AND DISCUSSION

The mean content of elements in the leaves and soils of *R. olympicus* were given in Table 1. We found significant difference among sample sites regarding examined element contents in soils except for Cr and generally the highest element concentrations were determined in soils taken from WRP ($P < 0.05$; Table 1). These findings point a contamination around this area produced by tungsten mining activities. The mean W content of soils varied within a broad scale ranging from 2.70 ± 0.31 and 1889.05 ± 101.35 mg/kg dry weight. The highest mean soil W content was found in the soils taken from waste removal pools and it was approximately 700-folds higher than the soils of Site I which was assumed to be unpolluted area. This value was also much above the limits ranging from 0.4 to 5 mg/kg dry weight [17]. The variation model of Fe, Mo, Zn, Cu, Cd, Pb, Mn, B, Co and Bi which is caused by mining activities in the soils was similar to W variation model (Table 1). The amounts of these elements in WRP soils were many times more than the unpolluted sites. For example, the mean Fe content in the soils of WRP is reached up 243863.2 ± 76752.4 mg/kg dry weight while it varied between 21459.1 ± 8664.2 mg/kg dry weight and up 9282.1 ± 1096.7 mg/kg dry weight in soils of unpolluted sites. Similarly, we determined highest Mn content in soils of WRP (8662.7 ± 1493.0 mg/kg dry weight) and this value is out of the range which is reported for Mn in uncontaminated soils (100-4000 mg/kg dry weight) [18].

In addition to soil element content, we also found significant difference among sample sites in terms of W, Fe, Mo, Zn, Mn and Bi content in the leaves of *R. olympicus* ($P< 0.05$; Table 1). Among these elements, leaf W, Bi and Zn contents increased depending on increased concentrations in soils. The enhanced W level in soils was reflected in the leaf W content of *R. olympicus*. Because the mean highest W content was determined in the leaves of plant samples taken from WRP (1.81± 0.72 mg/kg dry weight). The rising of W in the leaves may indicate the maintainance of tungsten transportation under the excesses W content in soils. Due to the high tungsten content which exceeds the W content of plants from uncontaminated soils (0.1 mg/kg dry weight) [19, 20], we can pay attention to the accumulation capacity of this species for W. A significant positive correlation between W content in the leaves of *R. olympicus* and soils support our thinking (Table 2). This indicates that the transportation of W in this species is not affected by increased external W content. The W accumulation capacities of some natural plant species spread on this area such as *Marrubium astracanicum*, *Anthemis cretica* and *Tricetum flavescens* were also reported by our previous studies [16, 21]. The behavior of Bi was similar to that of W. The mean leaf Bi content was highest in plant samples taken from WRP (0.34 ± 0.09 mg/kg dry weight) (Table 2) and there was significant positive difference correlation between Bi content in the leaves of *R. olympicus* and it's soils (Table 2). These results indicate that *R. olympicus* can able to uptake Bi and transport it to leaves under the presence of increased Bi in the environment. If we take into account these properties, this species can considered as a candidate for phytoremediation applications only for W and Bi contaminated soils on this area. But, it seems that *R. olympicus* not to suitable for cleaning up the soils contaminated by other heavy metal. On the other hand, it can undertake a significant role in these environmental conditions by restricting the entry of many heavy metals to food web.

CONCLUSIONS

Elemental composition of soils around the abandoned tungsten mining (Bursa, Turkey) was changed by mining activities generally leading to soil contamination. The elevated W, Bi and Zn concentrations in the soils are resulted in increased transportation of these elements in *R. olympicus* plants without detrimental effect. But, this tendency was not observed for some examined elements such as Mo, Zn, Cu, Cd, Pb and B. According to these results, this species can act as candidate phytoremediator for W and Bi.

Table 1. Mean values of the elements determined in the leaves and soils (mg/kg dry weight) of *Rumex olympicus* collected from unpolluted sites (site I and II) and the mine waste removal pool (site III) around the tungsten mine

Elements		**Sample Sites**		
		I	**II**	**III**
W	**Soil**	$2.70^{b} \pm 0.31$	$15.06^{b} \pm 2.63$	$1889.05^{a} \pm 101.35$
	Leaf	$0.31^{b} \pm 0.02$	$0.18^{b} \pm 0.04$	$1.81^{a} \pm 0.72$
Fe	**Soil**	$21459.1^{b} \pm 8664.2$	$9282.1^{b} \pm 1096.7$	$243863.2^{a} \pm 76752.4$
	Leaf	$9.9^{ab} \pm 2.3$	$5.\ 3^{b} \pm 0.9$	$12.5^{a} \pm 3.4$
Mo	**Soil**	$2.79^{b} \pm 1.09$	$5.47^{b} \pm 2.20$	$16.05^{a} \pm 4.13$
	Leaf	$0.79^{ab} \pm 0.23$	$1.26^{a} \pm 0.55$	$0.30^{b} \pm 0.04$
Zn	**Soil**	$86.7^{b} \pm 14.0$	$75.5^{b} \pm 24.9$	$2326.6^{a} \pm 1053.8$
	Leaf	$23.7^{ab} \pm 2.4$	$18.8^{b} \pm 2.1$	$48.9^{a} \pm 17.3$
Cu	**Soil**	$52.0^{b} \pm 6.0$	$97.7^{b} \pm 5.8$	$1008.9^{a} \pm 509.8$
	Leaf	$6.6^{a} \pm 2.3$	$5.4^{a} \pm 0.6$	$5.6^{a} \pm 0.9$
Cd	**Soil**	$0.18^{b} \pm 0.07$	$0.19^{b} \pm 0.03$	$14.55^{a} \pm 5.31$
	Leaf	$0.39^{a} \pm 0.21$	$0.17^{a} \pm 0.01$	$0.34^{a} \pm 0.08$
Pb	**Soil**	$11.88^{b} \pm 1.49$	$12.05^{b} \pm 1.06$	$133.78^{a} \pm 21.35$
	Leaf	$0.52^{a} \pm 0.14$	$0.44^{a} \pm 0.12$	$0.49^{a} \pm 0.18$
Mn	**Soil**	$342.4^{b} \pm 124.0$	$501.4^{b} \pm 203.3$	$8662.7^{a} \pm 1493.0$
	Leaf	$397.3^{b} \pm 59.9$	$660.7^{a} \pm 149.8$	$818.0^{a} \pm 41.7$
B	**Soil**	$25.6^{b} \pm 6.8$	$32.6^{b} \pm 23.4$	$148.6^{a} \pm 31.7$
	Leaf	$25.8^{a} \pm 9.1$	$17.7^{a} \pm 2.3$	$12.4^{a} \pm 0.6$
Co	**Soil**	$3.86^{b} \pm 0.17$	$2.76^{b} \pm 0.51$	$6.72^{a} \pm 1.49$
	Leaf	$0.16^{a} \pm 0.03$	$0.13^{a} \pm 0.03$	$0.12^{a} \pm 0.03$
Cr	**Soil**	$23.10^{a} \pm 10.52$	$8.63^{a} \pm 4.97$	$14.26^{a} \pm 0.54$
	Leaf	$1.03^{a} \pm 0.16$	$1.27^{a} \pm 0.57$	$0.81^{a} \pm 0.05$
Bi	**Soil**	$4.25^{b} \pm 2.76$	$9.76^{b} \pm 5.18$	$409.16^{a} \pm 65.70$
	Leaf	$0.05^{b} \pm 0.06$	$0.01^{b} \pm 0.01$	$0.34^{a} \pm 0.09$

Table 2. Simple Correlation Coefficients (r^2), significant levels (Possibility, *P*) and linear regression equations ($Y = a + bx$) between elemental contents of the soil samples and leaf (mg kg_{dw}^{-1}) of *Rumex olympicus* (n = 9, $P < 0.05$ significant correlation)

Elements	r^2	*P*	$Y = a + bx$
W	0.788	**0.001**	Leaf-W = 0.247072 + 0.000814 *x Soil-W*
Fe	0.283	0.132	Leaf-Fe = 7.650786 + 0.000017*x Soil-Fe*
Mo	0.319	0.113	Leaf-Mo = 1.144922- 0.044217*x Soil-Mo*
Zn	0.707	**0.004**	Leaf-Zn = 21.15924 + 0.011203 *x Soil-Zn*
Cu	0.001	0.935	Leaf-Cu = 5.811079 + 0.000084 *x Soil-Cu*
Cd	0.013	0.767	Leaf-Cd = 0.290921 + 0.002272*x Soil-Cd*
Pb	0.018	0.731	Leaf-Pb = 0.465919 + 0.000289 *x Soil-Pb*
Mn	0.508	**0.031**	Leaf-Mn = 516.3739 + 0.034389 *x Soil-Mn*
B	0.441	0.051	Leaf-B = 24.07809 - 0.078702 *x Soil-B*
Co	0.153	0.298	Leaf-Co = 0.159851 - 0.005712 *x Soil-Co*
Cr	0.191	0.240	Leaf-Cr = 1.315333 - 0.018178*x Soil-Cr*
Bi	0.902	**0.000**	Leaf-Bi = 0.032462 + 0.000715 *x Soil-Bi*

REFERENCES

1. Islam, R., Mamat, Y., Ismayil, I., Yan, M., et al. (2015). Toxicity of anthraquinones: differential effects of Rumex seed extracts on rat organ weights and biochemical and haematological parameters. Phytotherapy Research 29:777-784.
2. Samancioglu A, Sat IG, Yildirim E, Ercisli S, et al. (2016). Total phenolic and vitamin C content and antiradical activity evaluation of traditionally consumed wild edible vegetables from Turkey, Indian Journal of Traditional Knowledge 15: 208-213.
3. DalCorso G, Manara A, Furini A (2013). An overview of heavy metal challenge in plants: from roots to shoots. Metallomics 5:1117-1132.
4. Ovečka M, Takáč T (2014). Managing heavy metal toxicity stress in plants: Biological and biotechnological toolsManaging heavy metal toxicity stress in plants: Biological and biotechnological tools. Biotechnology Advances 32: 73-86.
5. Baker AJM, Brooks RR (1989). Terrestrial higher plants which hyperaccumulate heavy elements: a review of their distribution, ecology and phytochemistry. Biorecovery 1:81-126.
6. Rascio N, Navari-İzzo F (2011). Heavy metal hyperaccumulating plants: How and why do they do it? And what makes them so interesting? Plant Science 180:169-181.
7. Bulak P, Walkiewicz A, Brzeziǹska M (2014). Plant growth regulators-assisted phytoextraction. Biologia Plantarum 58:1-8.
8. Vasas A, Orbán-Gyapai O, Hohmann J (2015). The Genus *Rumex*: Review of traditional uses, phytochemistry and pharmacology. Journal of Ethnopharmacology 175:198-228.
9. Sedaghat R, Roghani M, Ahmadi M, Ahmadi F (2011). Antihyperglycemic and antihyperlipidemic effect of *Rumex patientia* seed preparation in streptozotocin-diabetic rats. Pathophysiology 18:111-115.
10. Süleyman H, Demirezer LO, Kuruüzüm-Uz A, Akçay F (2002). Gastroprotective and antiulcerogenic effects of *Rumex patientia* L. extract. Pharmazie. 57: 204-205.
11. Vondráčková S, Száková J, Drábek O, Václav T, Hejcman M, Müllerová V, Tustoš P (2015). Aluminium uptake and translocation in Al hyperaccumulator *Rumex obtusifolius* is affected by low-molecular-weight organic acids content and soil pH. Plos One10: e0123351
12. Fu S, Wei C, Lanhani L (2016). Characterizing the accumulation of various heavy metals in native plants growing around an old antimony mine. Human and Ecological Risk Assessment. 22:882-898.
13. Rehder H, Gökçeoğlu M, Gebauer G, Güleryüz G (1994) Die vegetation des Uludağ-Gebirges (Anatolien). Phytocoenologia 24:167-192.
14. Güleryüz G, Titrek E, Arslan H (1998). Nitrogen mineralization in the ruderal sub-alpine communities in Mount Uludağ, Turkey. European Journal of Soil Biology 44: 408-418.

15. Kovancı OB, Gencer NS, Kovancı B (2009). Lycaenid butterflies (Lepidoptera: Lycaenidae) of northwestern Turkey with notes on their ecology and current status. Revista Colombiana de Entomología 35: 275-282.
16. Güleryüz G, Erdemir US, Arslan H, Güçer Ş (2016). Elemental composition of *Marrubium astracanicum* Jacq. growing in tungsten-contaminated sites. Environmental Science and Pollution Research 23:18332-18342.
17. Kabata-Pendias A, Mukherjee AB (2007). Trace elements from soil to human. Springer-Verlag, Berlin Heidelberg
18. Lepp NW (1981). Effect of heavy metal pollution on plants, vol. 2, metals in the environment. Applied Science Publishers, London
19. Rodushkin I, Ödman F, Holmström H (1999) Multi-element analysis of wild berries from northern Sweden by ICP techniques. Sci Total Environ 231: 53–65.
20. Wilson B, Pyatt FB (2009). Bioavailability of tungsten and associated metals in calcareous soils in the vicinity of an ancient metalliferous mine in the Corbières Area, southwestern France. Journal of Toxicology Environmental Health A 72: 807-816.
21. Erdemir US, Arslan H, Güleryüz G, Güçer Ş (2017). Elemental Composition of Plant Species from an Abandoned Tungsten Mining Area: Are They Useful for Biogeochemical Exploration and/or Phytoremediation Purposes? Bulletin of Environmental Contamination and Toxicology 98: 299-303.

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QUANTITATIVE INDICATORS OF THE PROCESS OF THE SOIL EROSION CATCHMENT NAMELESS BROOK, WESTERN SERBIA

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ABSTRACT

This study involves the evaluation of soil erosion within in small catchment within the Kamenica catchment, part of the Zapadna Morava catchment.

As regards the initiation of the wearing away of soil particles from the catchment slope, standard methods were used to quantify soil erosion. The aim of this study was to evaluate erosion factors in the catchment area of the nameless brook, classified as a dry valleys and small flash flood. The annual erosion intensity is 105.62 m^3 km^{-2} of soil. Based on natural and anthropogenic factors, the nameless brook catchment area belongs to erosion category IV, weak intensity, mixed type, with the erosion coefficient of 0.25.

Key words: catchment, dry valleys and small flash flood, soil erosion intensity.

INTRODUCTION

Land degradation and soil loss are global events. Human induced pressures on natural ecosystems are still in progress, along with conservation efforts [1]. The main factor causing soil degradation worldwide is water erosion, which threatens 56% of the world's arable land [2].

Over 90% of the total land area in the Republic of Serbia suffers from different types and intensities of erosion [3]. The erosion process can have both direct and indirect impacts, inducing permanent soil disappearance. The calculated value of the total annual sediment yield suggests that some 16.0 cm of soil are annually eroded off the 21,000 ha of land in Serbia [4]. In the Republic of Serbia (Central Serbia), there are 1.221 million ha of eroded soil, and 36,000 ha are in a steady state, now [5].

Erosion has mostly affected strongly sloping, deforested or cultivated shallow soils on slopes, formed on impermeable geological substrates, due to the effects of intense rainfall and fluctuating air temperatures [4].

The tendency of air temperature to increase and of rainfall to decrease is quite evident in the region of Čačak [6]. Climate change leads to degraded soil physical properties, increases soil erodibility and reduces the protective role of vegetation.

The above factors cause intensification of both surface and deep-cutting processes of erosion.

Given the above, the objectives of this study are quantitative assessment of soil erosion induced by a range of factors and estimation of sediment yield in one part of the catchment area of the Kamenica River (part of the Zapadna Morava catchment), i.e. its subbasin the nameless brook, its first right-hand tributary.

MATERIALS AND METHODS

The nameless brook is located near Čačak (43^0 $53^{'}$ N; 20^0 $21^{'}$ E), Western Serbia, and belongs to the catchment of the Zapadna Morava river.

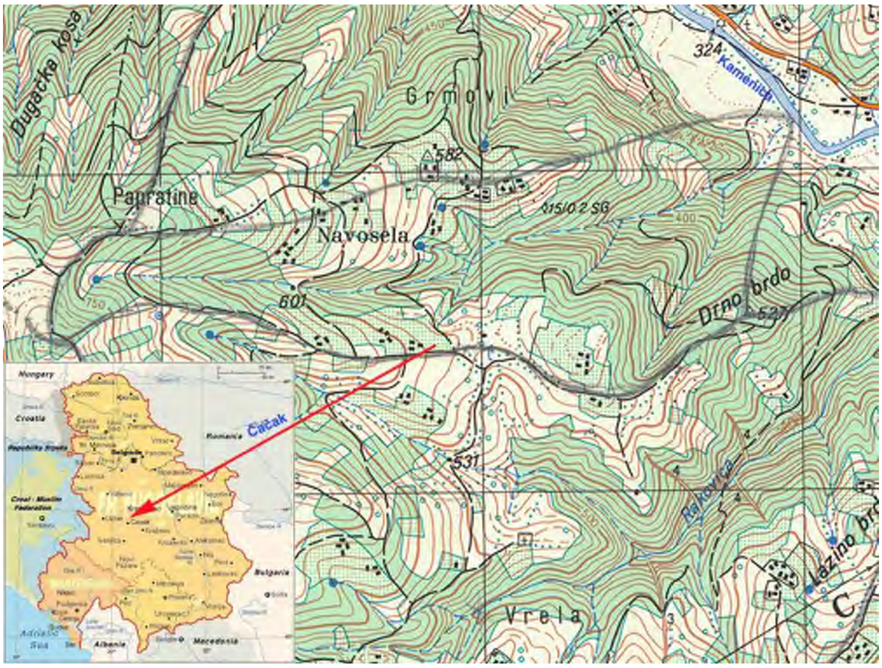

Figure 1. The nameless brook catchment

Natural characteristics of the nameless brook basin were studied using map data (hydrography, relief, geological substrate and soil), literature data (elements of climate: rainfall and air temperature) and data obtained through an immediate reconnaissance survey of the area (vegetation).

Maps of the studied area have the following scale: topographic map (1:25,000 Figure 1; 1:50,000) [7], geological map (1:500,000) [8] and pedological map (1:50,000) [9].

Meteorological parameters for the catchment area were calculated using the method of interpolation of rainfall data [10] by the rainfall gradient [11], and air temperature [12] calculations for any altitude [13].

Erosion-induced soil losses can be predicted by various analytical models.

However, according to the experience of a number of researchers, the Erosion Potential Method – EPM [14] is the most suitable on catchment level for watershed management purposes in this Region and is used in: Bosnia & Herzegovina, Bulgaria, Croatia, the Czech Republic, Italy, Iran, Montenegro, Macedonia, Serbia and Slovenia [15; 16; 17]. This is why quantitative indicators of soil erosion in this research were calculated using the Erosion Potential Method - EPM.

The basic analytical equation (1) for the calculation of erosion-induced soil losses, as developed [14], is as follows:

$$G_{yr \times sp^{-1}} = T \times H_{yr} \times \pi \sqrt{Z^3} \times R_u \qquad (1)$$

where:

- $G_{yr\ sp}^{-1}$ – specific annual total erosion-induced sediment yield reaching the confluence, $m^3\ yr^{-1}\ km^{-2}$
- T – temperature coefficient of the catchment
- H_{yr} – amount of rainfall, mm
- π – 3.14
- Z – coefficient of erosion
- R_u – coefficient of retention of soil in the catchment.

RESULTS AND DISCUSSION

The size, length, circumference and shape (perimeter) of a catchment area are among major catchment elements of importance for soil erosion. The nameless brook catchment is 1.06 km^2 in area (F), 2.20 km in length (L), and 5.60 km in circumference (C).

The major physical and geographical elements of the nameless brook catchment, relief characteristics, geological substrate features, soil type and soil utilisation method, are quantitative parameters or soil erosion in the catchment.

Table 1. The basic parameters of the nameless brook catchment relief

Catchment name: The nameless brook	
The lowest point of the main watercourse and catchment (B), m	319
The highest point of the main watercourse (C), m	725
The highest point of the catchment (E), m	795
Average slope of the main watercourse in the catchment (I_a), %	17.3
Mean catchment altitude (A_m), m	547.8
Mean catchment altitudinal difference (D), m	228.8
Mean catchment slope (I_m), %	29.5
Coefficient of catchment relief erosion energy (E_r), m km$^{-1/2}$	149.2

Table 1 presents the nameless brook relief which plays a primary role in the occurrence of soil erosion. The mean altitude (A_m) of the nameless brook is 547.8 m and the mean altitudinal difference (D) is 228.8 m. The mean slope (I_m) is 29.5%. Relief of a region can also be determined by the coefficient of relief erosion energy (E_r), the value thereof for the nameless brook catchment being 149.2 m $km^{-1/2}$. An increase in relief parameter values results in increasing intensity of soil erosion in the catchment.

Geological substrates contribute significantly to the erosion process within the nameless brook catchment area (Table 2). Erosion resistance of geological substrates is directly related to water permeability. The geological substrate of the nameless brook catchment is diabase (100.00% of the total catchment area) and is with poor permeability. The water permeability coefficient of the serpentine geological substrate (S_1) is 1.00, suggesting non-resistance of the geological substrate to the erosion process (Table 2).

Table 2. Geological substrate of the nameless brook catchment, coefficient of water permeability (S_1) and erosion resistance

Catchment name: The nameless brook		
F_{ppr}-Poorly permeable rocks		
• Diabase	km^2	1.06
	%	100.00
Coefficient of geological substrate water permeability (S_1)	1.00	
Resistance of geological substrate to erosion	Non-resistant	

As an erosion agent, soil and its properties contribute, to a lesser or greater degree, to the erosion process. Due to the effect of pedogenetic factors, the soil type covering the nameless brook catchment area is brown skeletal soil on diabase. It is classified as shallow soil. The profile of the brown skeletal soil on diabase is of A_h–C type. A strong degree of erodibility is found in the brown skeletal soil on diabase [18].

Table 3. The structure of the nameless brook catchment according to type of land use and vegetative cover coefficient (S_2)

Catchment name: nameless brook			
F_f	Forests and coppice of good spacing	km^2	0.64
		%	60.38
F_g	Orchards	km^2	0.10
		%	9.43
	Meadows	km^2	0.19
		%	17.93
	Pastures and devastated forests and coppices	km^2	0.10
		%	9.43
Σf_g		km^2	0.39
		%	36.79
F_b	Arable land	km^2	0.03
		%	2.38
	Infertile soil	km^2	0.00
		%	0.00
Σf_b		km^2	0.03
		%	2.83
Vegetation cover coefficient (S_2)		0.69	

The most aggressive climate elements inducing and contributing to soil erosion include rainfall, air temperature, and soil temperature (indirectly, through air temperatures). This region has a temperate continental climate. The mean annual rainfall total (R) for the nameless brook catchment is 808.2 mm, and the mean annual air temperature (T) is 7.9^{0}C. The data on rainfall reaching the catchment surface indicate an important role of rainfall as a climate element in soil erosion in the catchment area observed.

The contribution of the other soil erosion agents i.e. vegetation, both autochthonous and anthropogenic, and vegetative cover coefficient (S_2) is given in Table 3. The most of the land – 0.64 km^2 (60.38%) is under forests and coppice of good spacing, and 0.39 km^2 (36.79%) is under grass vegetation ($\sum F_g$) i.e. meadows 0.19 km^2 (17.93%), and orchards 0.10 km^2 (9.43%), and pastures and devastated forests and coppices 0.10 km^2 (9.43%), and 0.03 km^2 (2.38%) of the arable land, which is under bare soil ($\sum f_b$). These forms of land-use facilitate the protection of the studied area against erosion (vegetative cover coefficient, $S_2 = 0.69$).

The devastating potential of the watercourse can be determined from the hydrographic and hydrologic traits of the region analysed. The traits pertaining to the family of the nameless brook (F_c) are as follows: F_c: D; IV; Z=0.25, meaning that the nameless brook is a dry valleys and small flash flood (D) classified as class IV of erosion category (weak intensity of erosion) and having an erosion coefficient (Z) of 0.25 (mixed type of erosion).

The above traits of the erosion factors in the nameless brook catchment result in sediment production and soil erosion of particular intensity.

The scale of erosion of the nameless brook catchment is manifested through the mean annual erosion-induced sediment yield, W_{yr} of 302.59 m^3 yr^{-1}.

The mean annual volume of the total sediment yield (G_{yr}) reaching the nameless brook confluence is 111.96 m^3 yr^{-1}, whereas the specific annual total erosion-induced sediment yield reaching the confluence with the Kamenica River ($G_{yr\ sp}{}^{-1}$) is 105.62 m^3 km^{-2} yr^{-1}. This finding regarding the weak erosion intensity is comparable to that on the low-intensity erosion of the Grliška River region (Eastern Serbia) of ($G_{yr\ sp}{}^{-1}$) 209.12 m^3 km^{-2} yr^{-1} [19]. Using the method of EPM, in research of the Djuricka river basin (North of Montenegro), predicted that the soil losses were 645 m^3 km^{-2} per year [20].

The erosion intensity on the nameless brook catchment is manifested through the relief erosion energy coefficient of 149.2 m km$^{-1/2}$, the erosion coefficient (Z) of 0.25, mean annual rainfall of 757.6 mm and average annual air temperature of 9.0^{0}C, with about 60.38% under forests and coppice of good spacing, and 36.79% of land area under grass vegetation ($\sum F_g$), and 2.83% under bare soil ($\sum f_b$), and the dominating brown skeletal soil on diabase.

The above data show that, in view of the annual sediment yield, about 0.15 ha of soil up to 20 cm depth are eroded of the nameless brook catchment area i.e. about 0.23 t ha^{-1} of soil are lost annually. The amount of the eroded soil material can be categorised as class I (0-1 t ha^{-1} yr^{-1}) of permissible or tolerable erosion [1].

This model can be integrated with GIS technology for prediction of soil erosion and its spatial distribution [21].

CONCLUSION

The nameless brook is classified as a dry valleys and small flash flood. The value of Z coefficient of 0.25 indicates that the river basin belongs to destruction category IV. The strength of the erosion process is weak, and a mixed type erosion dominates in the studied area.

These and the other soil erosion agents analysed in the catchment area have resulted in the mean annual erosion-induced sediment yield of 302.59 m^3 yr^{-1}, and erosion intensity of 105.62 m^3 km^{-2} yr^{-1}. The erosion observed in this region is of weak intensity, and the anthropogenic factor is the key agent in the process governing soil utilisation, soil conservation and protection from further erosion-induced degradation.

Acknowledgement

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REFERENCES

1. Hacisalihoğly S., Mert A., Negiz Güvenç M., Muys B. (2010): Soil loss prediction using universal soil loss equation (USLE) simulation model in a mountainous area in Ağlasun district, Turkey. African Journal of Biotechnology, 9(24), 3589-3594.
2. Oldeman L. R., Hakkeling R. T. A., Sombroek W. G. (1990): World map of the status of human-induced soil degradation: an explanatory note. Second Edition, ISRIC Wageningen and UNEP, The Netherland.
3. Djorović M., Kadović R. (1997): Prospects for Development of conservation lands and waters. Proceedings of the Ninth Congress of the Yugoslav Association for the Study of land "Development, use and conservation of land," Hadzic V. (ed.), Yugoslav Society of Soil Science, 665-677, Novi Sad, Serbia. (In Serbian)
4. Spalević B. (1997): Erosion of Soil in the Federal Republic of Yugoslavia. Conservation of soil and water. Jakovljevic M. (ed.), Faculty of Agriculture, Belgrade-Zemun, Belgrade, Serbia. (In Serbian)
5. Statistical Yearbook (2008): Data on eroded areas of soil. Republic Institute for Statistics, Belgrade, Serbia. (In Serbian)
6. Šekularac G. (2002): The Tendency of Climatic Elements and Water Balance in the Soil of the Area of Cacak. Acta Agriculturae Serbica, VIII(14), 39–44.
7. Military Geographical Institute (1971): Topographic Maps (1:25,000; 1:50,000). Belgrade, Serbia. (In Serbian)
8. Institute of Soil Science (1966): Geological map of the western and north-western Serbia (1:500,000). Belgrade-Topcider, Serbia. (In Serbian)
9. Institute of Soil Science (1964): Soil map of the territory of the county of Kraljevo (1:50,000). Belgrade-Topcider, Serbia. (In Serbian)

10. Republic Hydrometeorological Bureau (1930-1961): Data on rainfall. Belgrade, Serbia. (In Serbian)
11. Bonacci O. (1984): Meteorological and hydrological data. Manual for Land Reclamation. I st, book 2, Tomic F. (ed.), Society for drainage and irrigation of Croatia, Zagreb, Croatia. (In Croatian)
12. Centre for Research in Agriculture (1949-1995): Data on air temperature. Čačak, Serbia. (In Serbian)
13. Dukić D. (1984): Physical and geographical factors of the river regime. Hydrology mainland. Joković D. (ed.), Science Book, Belgrade, Serbia. (In Serbian)
14. Gavrilović S. (1984): Engineering of torrential flows and erosion. "Building", Special Issue, Belgrade, Serbia. (In Serbian)
15. Behzadfar M., Tazioli A., Vukelic-Shutoska M., Simunic I., Spalevic V. (2014): Calculation of sediment yield in the S1-1 Watershed, Shirindareh Watershed, Iran. Agriculture and Forestry, 60(4), 207-216.
16. Spalevic V., Radanovic D., Behzadfar M., Djekovic V., Andjelkovic A., Milosevic N. (2014): Calculation of the sediment yield of the Trebacka Rijeka, Polimlje, Montenegro. Agriculture and Forestry, 60(1), 259-272.
17. Kostadinov S., Zlatic M., Dragicevic S., Novkovic I., Kosanin O., Borisavljevic A., Lakicevic M., Mlađan D. (2014): Anthropogenic influence on erosion intensity changes in the Rasina River watershed - Central Serbia. Fresenius Environmental Bulletin 01/2014; 23(1a), 254-263.
18. Šekularac G.: The ratio of the intensity of erosion and degree erodibility of soil of the Kamenica River (2000). Doctoral dissertation. University of Kragujevac, Faculty of Agronomy in Čačak, Čačak, Serbia. (In Serbian)
19. Stefanović T., Bilibajkić S., Braunović S., Nikić Z. (2007): State of erosion in the catchment Grliška River before and after the formation of the reservoir "Grlište". Water management, 39(5-6), 408-413. (In Serbian)
20. Spalevic V., Djurovic N., Mijovic S., Vukelic-Sutoska M., Curovic M. (2013): Soil Erosion Intensity and Runoff on the Djuricka River Basin (North of Montenegro). Malaysian Journal of Soil Science, 17, 49-68.
21. Tang Q., Xu Y., Bennett S. J., Li Y. (2015): Assessment of soil erosion using RUSLE and GIS: a case study of the Yangou watershed in the Loess Plateau, China. Environmental Earth Sciences, 73, 1715-1724.

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CONDITIONS FOR SOIL EROSION OF THE CATCHMENT OF THE NAMELESS BROOK (WESTERN SERBIA)

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ABSTRACT

This study involves the evaluation of soil erosion within in small catchment within the Kamenica catchment, part of the Zapadna Morava catchment.

As regards the initiation of the wearing away of soil particles from the catchment slope, standard methods were used to quantify soil erosion. The aim of this study was to evaluate erosion factors in the catchment area of the nameless brook, classified as a dry valleys and small flash flood. The annual erosion intensity is 75.43 m^3 km^{-2} of soil. Based on natural and anthropogenic factors, the nameless brook catchment area belongs to erosion category IV, weak intensity, surface type, with the erosion coefficient of 0.22.

Key words: conditions for soil erosion, dry valleys and small flash flood, catchment.

INTRODUCTION

Land degradation and soil loss are global events. Human induced pressures on natural ecosystems are still in progress, along with conservation efforts [1]. The main factor causing soil degradation worldwide is water erosion, which threatens 56% of the world's arable land [2].

Over 90% of the total land area in the Republic of Serbia suffers from different types and intensities of erosion [3]. The erosion process can have both direct and indirect impacts, inducing permanent soil disappearance. The calculated value of the total annual sediment yield suggests that some 16.0 cm of soil are annually eroded off the 21,000 ha of land in Serbia [4]. In the Republic of Serbia (Central Serbia), there are 1.221 million ha of eroded soil, and 36,000 ha are in a steady state, now [5].

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The tendency of air temperature to increase and of rainfall to decrease is quite evident in the region of Čačak [6]. Climate change leads to degraded soil physical properties, increases soil erodibility and reduces the protective role of vegetation.

The above factors cause intensification of both surface and deep-cutting processes of erosion.

Given the above, the objectives of this study are quantitative assessment of soil erosion induced by a range of factors and estimation of sediment yield in one part of the catchment area of the Kamenica River (part of the Zapadna Morava catchment), i.e. its subbasin the nameless brook, its first right-hand tributary.

MATERIALS AND METHODS

The nameless brook is located near Čačak (43^0 $53^{'}$ N; 20^0 $21^{'}$ E), Western Serbia, and belongs to the catchment of the Zapadna Morava river.

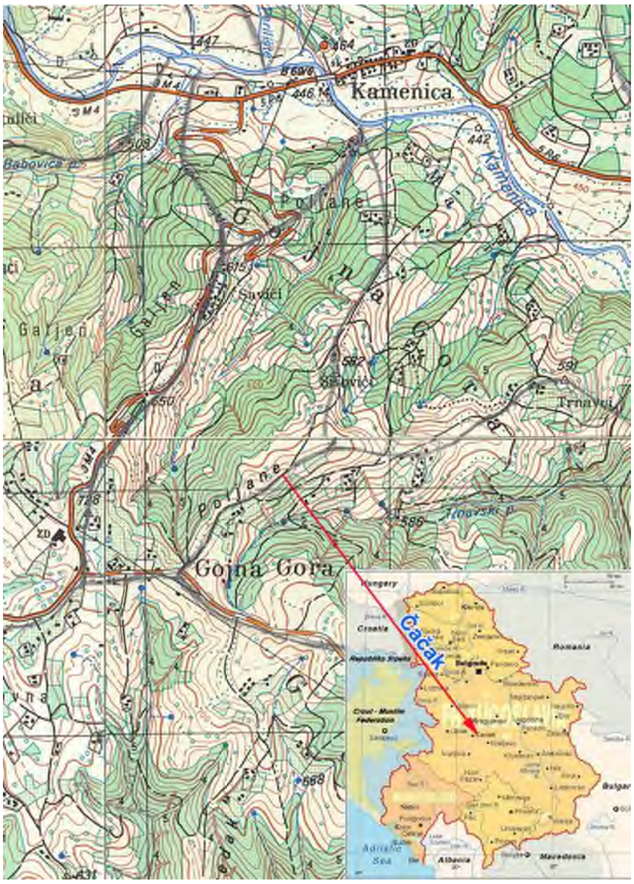

Figure 1. The nameless brook catchment.

Natural characteristics of the nameless brook basin were studied using map data (hydrography, relief, geological substrate and soil), literature data (elements of climate: rainfall and air temperature) and data obtained through an immediate reconnaissance survey of the area (vegetation).

Maps of the studied area have the following scale: topographic map (1:25,000 Figure 1; 1:50,000) [7], geological map (1:500,000) [8] and pedological map (1:50,000) [9].

Meteorological parameters for the catchment area were calculated using the method of interpolation of rainfall data [10] by the rainfall gradient [11], and air temperature [12] calculations for any altitude [13].

Erosion-induced soil losses can be predicted by various analytical models.

However, according to the experience of a number of researchers, the Erosion Potential Method – EPM [14] is the most suitable on catchment level for watershed management purposes in this Region and is used in: Bosnia & Herzegovina, Bulgaria, Croatia, the Czech Republic, Italy, Iran, Montenegro, Macedonia, Serbia and Slovenia [15; 16; 17]. This is why quantitative indicators of soil erosion in this research were calculated using the Erosion Potential Method - EPM.

The basic analytical equation (1) for the calculation of erosion-induced soil losses, as developed [14], is as follows:

$$G_{yr \times sp^{-1}} = T \times H_{yr} \times \pi \sqrt{Z^3} \times R_u \tag{1}$$

where:

$G_{yr\ sp}^{-1}$ – specific annual total erosion-induced sediment yield reaching the confluence, $m^3\ yr^{-1}\ km^{-2}$

T – temperature coefficient of the catchment

H_{yr} – amount of rainfall, mm

π – 3.14

Z – coefficient of erosion

R_u – coefficient of retention of soil in the catchment.

RESULTS AND DISCUSSION

The size, length, circumference and shape (perimeter) of a catchment area are among major catchment elements of importance for soil erosion. The nameless brook catchment is 1.00 km^2 in area (F), 1.62 km in length (L), and 5.00 km in circumference (C).

The major physical and geographical elements of the nameless brook catchment, relief characteristics, geological substrate features, soil type and soil utilisation method, are quantitative parameters or soil erosion in the catchment.

Table 1. The basic parameters of the nameless brook catchment relief.

Catchment name: The nameless brook	
The lowest point of the main watercourse and catchment (B), m	445
The highest point of the main watercourse (C), m	610
The highest point of the catchment (E), m	728
Average slope of the main watercourse in the catchment (I_a), %	8.2
Mean catchment altitude (A_m), m	612.64
Mean catchment altitudinal difference (D), m	167.64
Mean catchment slope (I_m), %	24.2
Coefficient of catchment relief erosion energy (E_r), m $km^{-1/2}$	89.56

Table 1 presents the nameless brook relief which plays a primary role in the occurrence of soil erosion. The mean altitude (A_m) of the nameless brook is 612.64 m and the mean altitudinal difference (D) is 167.64 m. The mean slope (I_m) is 24.2%. Relief of a region can also be determined by the coefficient of relief erosion energy (E_r), the value thereof for the nameless brook catchment being 89.56 m km$^{-1/2}$. An increase in relief parameter values results in increasing intensity of soil erosion in the catchment.

Geological substrates contribute significantly to the erosion process within the nameless brook catchment area (Table 2). Erosion resistance of geological substrates is directly related to water permeability. The geological substrate of the nameless brook catchment is diabase (100.00% of the total catchment area) and is with poor permeability. The water permeability coefficient of the serpentine geological substrate (S_1) is 1.00, suggesting non-resistance of the geological substrate to the erosion process (Table 2).

Table 2. Geological substrate of the nameless brook catchment, coefficient of water permeability (S_1) and erosion resistance.

Catchment name: The nameless brook		
F_{ppr}-Poorly permeable rocks		
• Diabase	km^2	1.00
	%	100.00
Coefficient of geological substrate water permeability (S_1)	1.00	
Resistance of geological substrate to erosion	Non-resistant	

As an erosion agent, soil and its properties contribute, to a lesser or greater degree, to the erosion process. Due to the effect of pedogenetic factors, the soil type covering the nameless brook catchment area is brown skeletal soil on diabase. It is classified as shallow soil. The profile of the brown skeletal soil on diabase is of A_h–C type. A strong degree of erodibility is found in the brown skeletal soil on diabase [18].

Table 3. The structure of the nameless brook catchment according to type of land use and vegetative cover coefficient (S_2).

Catchment name: nameless brook			
F_f	Forests and coppice of good spacing	km^2	0.32
		%	32.00
F_g	Orchards	km^2	0.05
		%	5.00
	Meadows	km^2	0.11
		%	11.00
	Pastures and devastated forests and coppices	km^2	0.32
		%	32.00
Σf_g		km^2	0.48
		%	48.00
F_b	Arable land	km^2	0.20
		%	20.00
	Infertile soil	km^2	0.00
		%	0.00
Σf_b		km^2	0.20
		%	20.00
Vegetation cover coefficient (S_2)		0.77	

The most aggressive climate elements inducing and contributing to soil erosion include rainfall, air temperature, and soil temperature (indirectly, through air temperatures). This region has a temperate continental climate. The mean annual rainfall total (R) for the nameless brook catchment is 766 mm, and the mean annual air temperature (T) is 8.6^0C. The data on rainfall reaching the catchment surface indicate an important role of rainfall as a climate element in soil erosion in the catchment area observed.

The contribution of the other soil erosion agents i.e. vegetation, both autochthonous and anthropogenic, and vegetative cover coefficient (S_2) is given in Table 3. The most of the land -0.48 km^2 (48.00%) is under grass vegetation ($\sum F_g$) i.e pastures and devastated forests and coppices 0.32 km^2 (32.00%), meadows 0.11 km^2 (11.00%), and orchards 0.05 km^2 (5.00%), and 0.32 km^2 (32.00%) is under forests and coppice of good spacing, and 0.20 km^2 (20.00%) of the arable land, which is under bare soil ($\sum f_b$). These forms of land-use facilitate the protection of the studied area against erosion (vegetative cover coefficient, $S_2 = 0.77$).

The devastating potential of the watercourse can be determined from the hydrographic and hydrologic traits of the region analysed. The traits pertaining to the family of the nameless brook (F_c) are as follows: F_c: D; IV; Z=0.22, meaning that the nameless brook is a dry valleys and small flash flood (D) classified as class IV of erosion category (weak intensity of erosion) and having an erosion coefficient (Z) of 0.22 (surface type of erosion).

The above traits of the erosion factors in the nameless brook catchment result in sediment production and soil erosion of particular intensity.

The scale of erosion of the nameless brook catchment is manifested through the mean annual erosion-induced sediment yield, W_{yr} of 235.71 m^3 yr^{-1}.

The mean annual volume of the total sediment yield (G_{yr}) reaching the nameless brook confluence is 75.43 m^3 yr^{-1}, whereas the specific annual total erosion-induced sediment yield reaching the confluence with the Kamenica River ($G_{yr\ sp}{}^{-1}$) is 75.43 m^3 km^{-2} yr^{-1}. This finding regarding the weak erosion intensity is comparable to that on the low-intensity erosion of the Grliška River region (Eastern Serbia) of ($G_{yr\ sp}{}^{-1}$) 209.12 m^3 km^{-2} yr^{-1} [19]. Using the method of EPM, in research of the Djuricka river basin (North of Montenegro), predicted that the soil losses were 645 m^3 km^{-2} per year [20].

The erosion intensity on the nameless brook catchment is manifested through the relief erosion energy coefficient of 89.56 m $km^{-1/2}$, the erosion coefficient (Z) of 0.22, mean annual rainfall of 766 mm and average annual air temperature of 8.6^0C, with about 48.00% under grass vegetation ($\sum F_g$), and 32.00% under forests and coppice of good spacing, and 20.00% of the arable land, which is under bare soil ($\sum f_b$).

The above data show that, in view of the annual sediment yield, about 0.12 ha of soil up to 20 cm depth are eroded of the nameless brook catchment area i.e. about 0.18 t ha^{-1} of soil are lost annually. The amount of the eroded soil material can be categorised as class I (0-1 t ha^{-1} yr^{-1}) of permissible or tolerable erosion [1].

This model can be integrated with GIS technology for prediction of soil erosion and its spatial distribution [21].

CONCLUSION

The nameless brook is classified as a dry valleys and small flash flood. The value of Z coefficient of 0.22 indicates that the river basin belongs to destruction category IV. The strength of the erosion process is weak, and a surface type erosion dominates in the studied area.

These and the other soil erosion agents analysed in the catchment area have resulted in the mean annual erosion-induced sediment yield of 235.71 m^3 yr^{-1}, and erosion intensity of 75.43 m^3 km^{-2} yr^{-1}. The erosion observed in this region is of weak intensity, and the anthropogenic factor is the key agent in the process governing soil utilisation, soil conservation and protection from further erosion-induced degradation.

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REFERENCES

22. Hacisalihoğly S., Mert A., Negiz Güvenç M., Muys B. (2010): Soil loss prediction using universal soil loss equation (USLE) simulation model in a mountainous area in Ağlasun district, Turkey. African Journal of Biotechnology, 9(24), 3589-3594.
23. Oldeman L. R., Hakkeling R. T. A., Sombroek W. G. (1990): World map of the status of human-induced soil degradation: an explanatory note. Second Edition, ISRIC Wageningen and UNEP, The Netherland.
24. Djorović M., Kadović R. (1997): Prospects for Development of conservation lands and waters. Proceedings of the Ninth Congress of the Yugoslav Association for the Study of land "Development, use and conservation of land," Hadzic V. (ed.), Yugoslav Society of Soil Science, 665-677, Novi Sad, Serbia. (In Serbian)
25. Spalević B. (1997): Erosion of Soil in the Federal Republic of Yugoslavia. Conservation of soil and water. Jakovljevic M. (ed.), Faculty of Agriculture, Belgrade-Zemun, Belgrade, Serbia. (In Serbian)
26. Statistical Yearbook (2008): Data on eroded areas of soil. Republic Institute for Statistics, Belgrade, Serbia. (In Serbian)
27. Šekularac G. (2002): The Tendency of Climatic Elements and Water Balance in the Soil of the Area of Cacak. Acta Agriculturae Serbica, VIII(14), 39–44.
28. Military Geographical Institute (1971): Topographic Maps (1:25,000; 1:50,000). Belgrade, Serbia. (In Serbian)
29. Institute of Soil Science (1966): Geological map of the western and north-western Serbia (1:500,000). Belgrade-Topcider, Serbia. (In Serbian)
30. Institute of Soil Science (1964): Soil map of the territory of the county of Kraljevo (1:50,000). Belgrade-Topcider, Serbia. (In Serbian)

31. Republic Hydrometeorological Bureau (1930-1961): Data on rainfall. Belgrade, Serbia. (In Serbian)
32. Bonacci O. (1984): Meteorological and hydrological data. Manual for Land Reclamation. I st, book 2, Tomic F. (ed.), Society for drainage and irrigation of Croatia, Zagreb, Croatia. (In Croatian)
33. Centre for Research in Agriculture (1949-1995): Data on air temperature. Čačak, Serbia. (In Serbian)
34. Dukić D. (1984): Physical and geographical factors of the river regime. Hydrology mainland. Joković D. (ed.), Science Book, Belgrade, Serbia. (In Serbian)
35. Gavrilović S. (1984): Engineering of torrential flows and erosion. "Building", Special Issue, Belgrade, Serbia. (In Serbian)
36. Behzadfar M., Tazioli A., Vukelic-Shutoska M., Simunic I., Spalevic V. (2014): Calculation of sediment yield in the S1-1 Watershed, Shirindareh Watershed, Iran. Agriculture and Forestry, 60(4), 207-216.
37. Spalevic V., Radanovic D., Behzadfar M., Djekovic V., Andjelkovic A., Milosevic N. (2014): Calculation of the sediment yield of the Trebacka Rijeka, Polimlje, Montenegro. Agriculture and Forestry, 60(1), 259-272.
38. Kostadinov S., Zlatic M., Dragicevic S., Novkovic I., Kosanin O., Borisavljevic A., Lakicevic M., Mlađan D. (2014): Anthropogenic influence on erosion intensity changes in the Rasina River watershed - Central Serbia. Fresenius Environmental Bulletin 01/2014; 23(1a), 254-263.
39. Šekularac G.: The ratio of the intensity of erosion and degree erodibility of soil of the Kamenica River (2000). Doctoral dissertation. University of Kragujevac, Faculty of Agronomy in Čačak, Čačak, Serbia. (In Serbian)
40. Stefanović T., Bilibajkić S., Braunović S., Nikić Z. (2007): State of erosion in the catchment Grliška River before and after the formation of the reservoir "Grlište". Water management, 39(5-6), 408-413. (In Serbian)
41. Spalevic V., Djurovic N., Mijovic S., Vukelic-Sutoska M., Curovic M. (2013): Soil Erosion Intensity and Runoff on the Djuricka River Basin (North of Montenegro). Malaysian Journal of Soil Science, 17, 49-68.
42. Tang Q., Xu Y., Bennett S. J., Li Y. (2015): Assessment of soil erosion using RUSLE and GIS: a case study of the Yangou watershed in the Loess Plateau, China. Environmental Earth Sciences, 73, 1715-1724.

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CORROSION OF METALS IN SOIL – REVIEW

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ABSTRACT

This paper presents a literature review of soil pollution due to metal corrosion. Soil and groundwater are dynamic systems that are in balance with the environment and it is necessary to continuously monitor their condition. Migration of pollutants through the soil depend on the conditions of the environment (soil mechanical characteristics of the soil), the type of pollutants and their physical - chemical properties, as well as the status of the groundwater. From harmful substances which appear in the soil and groundwater in a landfill, for the most part are present the heavy metals and complex mixtures of hydrocarbons as a result of the inadequate treatment of waste.

Key words: soil pollution, corrosion, heavy metals, groundwater.

INTRODUCTION

Intensive urbanization, industrial development, transport and agricultural activities lead to excessive pollution of the environment, including land. Among the most important contaminants is one of petrochemical industries, which creates large amounts of waste, toxic materials in the solid or liquid state [1]. One of the main soil pollutants are heavy metals, which are found naturally in soil, in certain concentrations, and descended from the parent rock. Pollution of the soil metals is significantly different from air pollution or water in the fact that the heavy metals in the soil retained much longer than in other layers of the biosphere [2]. Metals which have a bulk density greater than 5 g/cm^3 belong to the group of heavy metals. Heavy metals (lead, cadmium and copper) are widespread in the environment. Their representation as pollutants in the working environment is a serious health and environmental problems because they are toxic, non-biodegradable, have a very long half life in the soil and accumulate in the living system through activated food chain [3]. In addition to the negative influence of climatic conditions on the corrosion resistance alloy with bacteria and fungi. They contribute to the process of rapid corrosion or greater mobility and the bioavailability of metal ions [4].

THE COMPOSITION AND CAUSES SOIL POLLUTION

Sources of soil pollution are the consequences of human activities and basically can be divided into three groups:

- Waste water such soil pollutants (industrial waste water contaminated with agricultural activity, domestic waste water)
- The atmospheric pollutants which contaminate soil washing, precipitation or sedimentation by direct (emissions from industrial technological processes, emissions due to the burning of fossil fuels, emissions during the burning of many organic materials) and
- Solid waste of various origins (municipal waste, industrial waste, waste from agriculture, heavy metals).

In Table 1, it indicates the average elemental composition of the lithosphere of the soil, the surface of the lithosphere.

Table 1. The mean content of the chemical elements in the lithosphere and soil percentages by weight [5]

Elements	Lithosphere	Soil	Elements	Lithosphere	Soil
O	47.2	49.0	C	(0.1)	2.0
Si	27.6	33.9	S	0.09	0.085
Al	8.8	7.13	Mn	0.09	0.085
Fe	5.1	3.8	P	0.08	0.08
Ca	3.6	1.37	N	0.01	0.1
Na	2.64	0.63	Cu	0.01	0.002
K	2.6	1.36	Zn	0.005	0.005
Mg	2.6	1.36	Co	0.003	0.0008
Ti	0.6	0.46	B	0.0003	0.001
H	(0.15)	/	Mo	0.0003	0.0003

When contaminants have entered the plot in any of these ways, its subsequent fate depends on a number of physical, chemical and biological factors whose effects are intertwined. Also very important is in the form of a compound which these contaminants are, as well as the characteristics of the land (the vegetation, processing, climate) [6], [7].

HEAVY METALS IN SOIL

The heavy metals or toxic, are among metals whose density is greater than 5 g/cm³. The toxic metals are among those metals which are not biogenic and act solely as toxic as cadmium, lead, mercury, arsenic, thallium and uranium. Heavy metals have multiple importance, they are an important raw material for many industries, some of them are essential for living organisms, can act favorably on the productivity of agriculture and most of them are often a significant polluter of the environment. Toxic metals are among the most dangerous contaminants and present a major threat to all living organisms, in particular humans and animals [8].

RESEARCH RESULTS

Corrosion can be defined as material degradation due to reactions with its surroundings. Degradation means the deterioration of the physical properties of materials. This may be due to the weakening of the material cross-sectional area of losses, may be due to its breaking metal embrittlement or cracking. The materials may be metals, polymers, ceramics. Metals are the most common type of structural material. Metals corrode because we use them in areas where they are chemically unstable. Only copper and precious metals are found in nature in such a state, all the others are processed from minerals or metal ores which are unstable in their communities. All other metals are unstable and tend to return to their stable forms. Some metals fomira protective ceramic films that can slow or prevent corrosion. There are several forms of corrosion such as uniform, galvanic, pitting corrosion and others. [9].

In the assessment of its potential risks of corrosion and heavy metal load in the environment-induced corrosion, it is important to distinguish between korzije and swelling. Swelling of the quantity of metal that is due to rainfall washed from the surface while the corrosion of the total amount of metal that is oxidized. During the process of corrosion of heavy metal are formed by the corrosion products according to the following equations [10]:

$$Zn\ (s) \rightarrow Zn^{2+} + 2e^- \quad (1)$$
$$Cu\ (s) \rightarrow Cu^{2+} + 2e^- \quad (2)$$
$$Pb\ (s) \rightarrow Pb^{2+} + 2e^- \quad (3)$$
$$Hg\ (s) \rightarrow Hg^{2+} + 2e^- \quad (4)$$
$$Cr\ (s) \rightarrow Cr^{2+} + 2e^- \quad (5)$$

In the process of wet corrosion (high water content of the soil), electrons generated from the anode are moved corrosive to the cathode where it recombines with the intervening oxygen and water in the electrolyte to make a new hydroxyl ion. This new negative charge ions reacted so that trying to make sabilna compounds with positive metal ions. In this case, electrons have a continuous path from the base metal, which can not develop a protective barrier and then distances itself or breakup. When corrosion starts this continues until the ingredients are not spent [10].

In recent decades, more and more talk about new pollutants - depleted uranium (DU), which is used in anti-tank penetrators due to its high density, penetration and pyrophoric properties. It is estimated that during the NATO aggression in the former Yugoslavia in 1999 about 10 tons of depleted uranium introduced into the environment, mainly in the agricultural in. At the time of these events has been very little information available about the behavior of ecosystems degraded remnants of DU penetrators. Today, after fourteen years, are increasingly faced with - the invisible threat of the use of DU ammunition, which has a strong radioactive and hemotoxic impact on human health. Various authors studied the corrosion and environmental behavior DU, along with indicators of environmental impact, with the aim to highlight areas that need further attention in the development of remediation programs. Natural sources of uranium in Serbia (NORM) are igneous sedimenentne, carbonate rocks and granite, in the average content of up to 3.5 GU / t and as "background of the natural level of ionizing radiation." Naturally increased content of uranium is found in mountainous regions, Bukulje, the Lamb, Old Mountains, Avala- Kosmaj, Coal, Cer, Vranje, Fruška Gora and Vrsac hill, on the average of 50-200 Bq/kg. Technological processes in power plants, reprocessing phosphate, production and use of phosphate fertilizers, residues DU ammunition represent the main form of TENORM. Thus, in the vicinity of "Kolubara" and "Nikola Tesla", strength of an equivalent dose of radiation ranges from 1.42 to 4.87 nSv/h, which is 3 to 4% higher than the level of natural radiation. The production and use of phosphate fertilizers contributes significantly to increasing the content of uranium in the environment and global character. Around 73% of the anthropogenic input of uranium in the environment on a global scale, originating from the phosphate mineral fertilizers. The content of phosphate ores of uranium and can reach up to 300 g/t, according to its origin. Based on the world's annual consumption of about 135 million tons of phosphate ore with an average content of about 150 g/t, it is estimated that their processing can bring about 21,000 t of uranium in the environment. Based on the data that in Serbia annually on fields bring about 1 million tons of fertilizers based on phosphorus, it is estimated that with these amounts of imports into the environment of more than 200 t of uranium. Abandoned mines and uranium deposits are significant generators of uranium tailings thus closed in a uranium mine Gabrovnica-Kalna, containing 15,33 mg U/kg to 17 mg U/kg. The water emanating from the mine and today, containing 0.053 mg of In/dm^3 of water. Vegetation experiments in real and controlled conditions with different types of plants (crops and vegetables), showed that the content of uranium in plants grown on tailings in Kalni significantly higher than the content of uranium in plants grown on uncontaminated soil, and the degree of adoption of uranium, depends on the type of plant genotypes and plant organs. According to some estimates, a "natural level of ionizing radiation" in some areas Serbia has increased 30 times in the last 30 years, caused by human activities. Unfortunately, the contribution TENORM in Serbia was the use of depleted uranium during the NATO bombing in 1999 which is the subject of further exposure. Migration potential of uranium depends on the physico-chemical properties of soil and the soil solution and the oxidation product DU. To the mobility of the dissolved products of uranium, predominantly affected by the pH, and the presence of complexing agents of organic or inorganic in the local ground water and soil. Hexavalent uranium, exist in solution as uraniljon (DO22 +) and it is more mobile because of U readily form water-soluble complexes with the ligands present in the soil solutions. It has been shown that the presence of carbonate and phosphate, also affects these processes. Transportation of a soluble form of uranium can be accelerated by diluting, since it reduces its concentration in the surface and underground waters. These reactions include ion exchange and adsorption specific uranium [11].

CONCLUSION

Scientists have contributed to the understanding of the processes and factors that control the corrosion of depleted uranium and transport of corrosion products penetrators through the environment. The formation of aerosol DU penetrators DU during the interaction with solid target, is the dominant route of environmental contamination by air transport and a major threat to human health. Put contamination of these particles depends primarily on the atmospheric conditions. Corrosion penetrators DU is a complex process, specific to each site and takes place in the interaction of chemical, physico-chemical and biogeochemical processes. The dominant factors affecting the corrosion of the pH and the redox potential, geomorfološka body soil, the concentration and types of inorganic and organic compounds in the soil, soil temperature, pressure, moisture content, microbial and fungicidal activity, micro soil fauna, salinity. These same factors will affect the dissolution of the corrosion products. The conclusion is that every contaminated site is a specific case and requires extensive monitoring and multidisciplinary approach to rehabilitation. The task of all of us is that the devastating effects of depleted uranium minimize and prevent its penetration into the food chain.

Phytoremediation is an interdisciplinary technology. So far, the results have shown that certain plants can be effective in remediation of heavy metal contaminated soil.

REFERENCES

1. T. Radić-Lakoš, M. Radačić, Usage of hyperaccumulation of heavy metals in polluted soil remediation, Transport and contemporary condition of management 6 (2010) 335-342
2. V. O. Sing, S. Labana, G. Pandey, R. Budhiraja, K. R. Jain, Phitoremediation: an overview of metallion decontamination from soil, Applied Microbiology and Biotechnology 61 (2003) 405-412
3. Health and environment in sustainable development, Geneva: WHO 1997
4. M. Yan, C. Sun, J. Xu, J. Dong, W. Ke, Role of Fe oxides in corrosion of pipeline steel in a red clay soil, Corrosion Science 80 (2014) 309–317
5. Mansell, R. When, U (editors): Knowledge Societies: Information Technology for Sustainable Development. Oxford (UK): Oxford University Press, 2008.
6. M. Ilić, S. Miletić, Fundamentals of Solid Waste Management, Belgrade, 1998.
7. D. Damjanović, The main criteria in determining the engineering-geological and hydrogeological conditions when planning the location for hazardous waste disposal, Faculty of Engineering, Novi Sad, 2008.
8. C. Fernandez, F. Monna, J. Labanowski, M. Loubet, F. van Oort, Anthropogenic lead distribution in soils under arable land and permanent grassland estimated by Pb isotopic compositions, Environmental Pollution 156 (2008) 1083–1091
9. M. Arpaia, P. Pernice, A. Costantini, Kinetic mechanism of steel corrosion in clay soils by impedance measurements, Materials Chemistry and Physics 24 (1990) 373-382
10. W. Gerwin, R. Baumhauer, Effect of soil parameters on the corrosion of archaeological metal finds, Geoderma 96 (2000) 63–80
11. M. D. Stojanović, Č. M. Lačnjevac, M. L. Mihajlović, M. V. Petrović, T. D. Šoštarić, J. T. Petrović, Z. R. Lopičić, Organic and corrosion behavior of depleted uranium Review Work (2014)

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POSITIVE EFFECTS OF WASTE WATER TREATMENT PLANT CONSTRUCTION ON THE ENVIRONMENT WITHIN KICEVO MUNICIPALITY

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ABSTRACT

This thesis contains elaboration of the sewage system for the observed agglomeration area and reconstruction of the existing sewage system within the city of Kičevo. Special attention was paid to the selection of water treatment methods and then for actual designing of water treatment plant. The goal of this thesis is to show significance of construction of the WWTP (Waste Water Treatment Plant) for improvement environmental and living conditions in Kičevo Municipality.

Key words: sewage system, water treatment plant, environmental protection, quality life improvements.

OVERVIEW

The Municipality of Kičevo is located in the south-western part of Macedonia and is situated in the Kičevo Valley that presents clearly a shaped natural area, surrounded on all sides by high mountains. Kičevo Valley belongs to the upper region of the Treska River, on the north side it reaches to the overpass Straška, on the west side it touches the Mountain Bistra, on the south side it extends to the Ilinska Mountains and on the east side it touches the north part of Poreče region.

Five municipalities are merged into the Municipality of Kichevo with the administrative changes in 2013. Accordingly to actual territorial division the Municipality comprises of the following settlements: Zajas, Oslomej, Kičevo, Drugovo, and Vraneštica and surrounding villages. In accordance with projection of population, the total number of inhabitants in the municipality is 57,153 at the end of year 2014 [1]. The Municipality of Kičevo covers an area of 838 km^2.

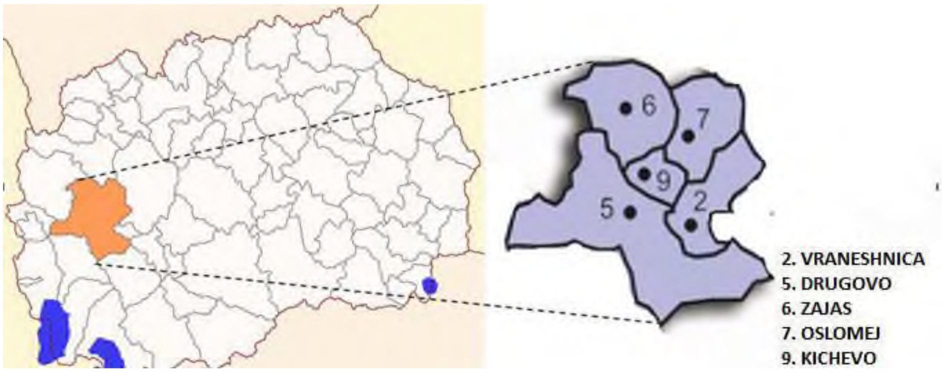

Figure 1. Location of the Municipality of Kičevo with settlements

The main administrative and business (urban) center in the region is the town of Kičevo, situated at 620-650 meters above sea level. Kičevo town is also the largest settlement in the region with population of approximately 30,500 (including surrounding rural parts) inhabitants.

Through the central part of the Kičevo town, flows the river Sušica, tributary of the river Zajaska. The river Zajaska runs downstream through Kičevo, separating the town in two parts connected by a bridge; after few kilometers it flows into the river Treska. The Treska River is a major tributary of the Vardar River and is considered as a valuable water resource in the country.

Public Enterprise "Komunalec" (PE "Komunalec") is responsible for distribution of portable water and collection and disposal of wastewater, including maintenance and development of the water supply and wastewater networks.

The town of Kičevo is supplied with portable water by the regional water supply system "Studenčica".

The total capacity of the "Studenčica" system is approximately 1,500 l/s with a reduction during the summer months. In accordance with "FS-2015" (Feasibility Study – 2015) [2] Kičevo receives on average some 260 l/s of water from this system. The pipeline supplying Kičevo from the "Studenčica system" is about 6 km in length.

Water quality from the water supply system "Studenčica" is of acceptable quality.

Disinfection of water is conducted in chlorinating station.

Control of water quality from water sources is the responsibility of PE "Komunalec".

In accordance with the "FS-2015" [2], most of the results of testing are within the standards required by the law, except on rare occasions. These occasions occur mostly in the summer when the drinking water quality standards are not met. In these instances the regional Public Health Institute issues warnings requesting people to boil their water before consumption.

Major pollution sources originate from direct discharge of domestic and industrial/commercial/institutional wastewater prior any treatment into the watercourses.

Collected wastewater from the town of Kičevo is discharged directly into the recipients. In accordance with the "FS-2015" [2], there is nine discharge points along the Zajaska River. However, during geodetic survey of sewerage network, 14 discharge points (outlets) into the Zajaska River were found.

Besides that, another major pollution source is the municipal waste landfill that is located on the bank of Zajaska River, about 260 m north of location of planned WWTP. The landfill has no protection measures and leachate enters the river causing serious pollution. The Project for Regional Waste Management and Landfilling, financed by IPA (Instrument for Pre-Accession Assistance) 2, which will include dislocation of the existing municipal landfill and revitalisation of the site is foreseen to be implemented in the short term.

According to the information received by PE "Komunalec", the percent of population connected to the local wastewater sewerage systems in the Project area varies dependent on development of sewerage in settlements/villages. It is assessed that approximately 63% of population within Project Area is connected to the wastewater sewerage systems.

Population not connected to the wastewater system mainly uses individual septic tanks.

Impact on groundwater is significant in areas not covered by the wastewater sewerage system and in areas partially covered by the wastewater system.

Presence of a large number of outlets of untreated wastewater into the watercourses presents a constant environmental pressure due to the pollutant load.

OBJECTIVES OF ANALYSIS OF OPTIONS

Objectives of this analysis of options is to determine the most efficient way to connect settlements which are situated in the Project Area to wastewater collection system and consequently to the treatment plant, taking into account financial and technical feasibility.

Through the "FS-2015" [2] capacity of the WWTP Kičevo and type of treatment process which will be implemented, based on comprehensive analysis was determined.

This Feasibility Study is developed on the basis of calculation of population projection and calculation of wastewater flows and loads, but keeping the outcomes of previously prepared and approved documentation [2, 3]. Waste water treatment was implemented according to EU Directives.[4][5][6]

Main outcomes of already approved documentation that are obligatory for this Feasibility Study are the following:

- main collector [7]
- location of the WWTP Kičevo
- total capacity of the WWTP Kičevo is 48,000 population equivalent.

ENVIRONMENTAL REVIEW OF PROPOSAL

The overall project (rehabilitation and extension of sewerage and construction of the WWTP Kičevo)[3] will have a significant beneficial impact through the removal of environmental pollution (pollution of surface water and groundwater) and consequently will reduce risks to public health. Without the project, significant adverse risks to public health would continue and deteriorate.

In addition, realization of the project will enable the treatment of collected wastewater after construction of WWTP Kičevo[3], which will improve the water quality of the rivers Zajaska and Treska downstream of the town Kičevo.

The direct and indirect effects of the project have been assessed with regard to the following:

- Human beings
- Fauna and flora
- Soil, water, air, climate and the landscape
- Material assets and cultural heritage.

Human Beings

Potential impacts comprise the following:

- Socio-economic impacts (labor, land purchase and compensation, welfare, severance)
  The socio-economic impacts of the project are considered to be moderately positive. The proposed upgrading of the existing sewerage network will result in local employment opportunities during the construction phases. Nevertheless, the impact is likely to be positive.

- Nuisance due to noise, odor, dust, light pollution, wind-blown litter, pests and vermin
  Some degree of disruption will arise in the course of the proposed construction work of the sewerage. This will have a temporary negative impact on visual amenity and, in some instances on traffic in populated areas. However it is also of importance to note that the project provides the opportunity to enhance the existing landscape and visual amenity. Improvements that are being considered, while still maintaining the existing landscape, including clearing the area from rubbish and debris. Visual amenity is unlikely to be an issue in respect of the wastewater collection and transport constructions associated with the priority investment plan, since the majority of the assets will be underground. The impact related to odor during construction of sewers is assessed as negligible. Construction work will result in significant, but temporary increase in noise levels. This needs to be addressed via adequate mitigation measures.

- Traffic & access and associated disruption
  The sewers being laid within the boundaries of the town and settlements will result in a significant level of disruption, which will present a minor to moderate

negative impact. Adequate mitigation measures will need to be adopted. The additional traffic which will arise during the construction phase will result in a local increase in traffic volumes which will present a minor negative impact. However this impact can be mitigated as described below. Once operational the likely traffic movements will be low.

- Health & safety
  During the construction phase of the project a wider range of health and safety issues arise, particularly from the construction of new underground infrastructure in the town centre. Measures will include traffic control and road safety issues. The application of construction codes of practice and other similar measures will be incorporated into the project specification so as to minimize the adverse impact of these works. After completion of works, discharges of wastewater into the river will be closed and consequently hygienic standard of population will be improved.

Flora and Fauna

The project will not have any negative impact to any nature protected areas.

Soil, Water, Air, Climate and the Landscape

- Soil, Geology, Hydrogeology
  Land take associated with the sewerage network will not be extensive, impacts at those locations on soil resources are considered to be minor. However, negative impacts could arise in green areas of the town in the course of excavations for underground assets. In accordance with good practice, top soil from these excavations will be required to be conserved and reused for backfilling and reinstatement.
- Waste Management
  Waste arising from the implementation phase of the project needs to be considered. As part of the construction and demolition works, waste will be generated and will need to be disposed of. In some areas of the town this could possibly include contaminated soil. Arrangements for identifying such waste and its safe removal and disposal will need to be determined. Other than possible areas of existing contaminated land, the majority of waste which will occur during the construction phase will be inert, which can be used for infill. Other materials which are not suitable for such use, including broken pipes and fittings will need to be separated and disposed of, as appropriate, to the existing landfill. Material containing asbestos has been observed during the site reconnaissance. Asbestos is classified as a hazardous waste and should be handled according to the special requirements set for its management and disposal. Procedures for asbestos handling in Macedonia have not been evaluated. Nevertheless, precautions in accordance with Directive 83/477/EEC5[4] should be followed. Moreover, disposal should be to a suitably

authorized facility. Currently the asbestos waste is being sent abroad for utilization. It is recommended that any asbestos removal work is only started once a suitable authorized disposal location has become available.

- Surface water
  In addition, by closing discharges of wastewater into the water streams and treatment of wastewater will improve quality of waters in rivers. The project includes closing of wastewater outlets in the river Zajaska in the center of the town of Kičevo, as well as other existing discharges into the water streams of local sewerage systems in villages. Closing of discharges of wastewater into the water streams and treatment of wastewater (after construction of the WWTP Kičevo)[3] will improve quality of waters in rivers.

- Groundwater quality
  Whilst quantitative analysis of the impact of the project on groundwater quality has not been possible, it is clear that the project will have a positive impact on groundwater quality. Choice of proper material for the construction of new trunks provides impermeability of pipes and thus protects groundwater of pollution.
- Air Quality and Climate
  Operation of the sewerage networks does not generally give rise to significant emissions to air other than those associated with energy use. In the construction phase the main sources of pollution will arise from traffic, construction dust and combustion. Their impact is not considered to be major, but mitigation measures should be employed. Traffic will comprise delivery of materials, construction equipment and construction workers. It is however considered that traffic will have a negligible effect on air quality in the town and settlements given the existing levels of pollution arising from other sources – i.e. existing traffic, domestic heating and industry. Dust can arise from vehicle movements and material stockpiles. However, the scale of works is such that this should not be significant. Any excavated material is likely to be wet so large amounts of wind-blown dust are not anticipated. This consideration will be of particular importance during construction works within the urbanized areas of town. Combustion emissions (SO_2, CO_2, NOx) will arise from bulldozers, cranes, excavators and to avoid unnecessary emissions and energy usage their engines should be shut down while the machinery is idle.

Material assets and cultural heritage

The construction of the sewer networks and associated works within the project area has the potential to uncover buried remains of archaeological interest. No evidence has come to light to suggest that there are any historic remains at the locations of the wastewater sewers, it is not therefore proposed that any pre-construction excavations be made for archaeological purposes.

CONCLUSION

Construction of WWTP Kičevo will contribute to the living conditions of the local community. The direct and indirect effects of the project have been assessed with regard to the following: human beings; fauna and flora, soil, water, air, climate and the landscape and material assets and cultural heritage. Decrease of negative effects on the environment will be accomplished through better water supply and water treatment.

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REFERENCES

1. "Statistical Review – Population and Social Statistics" (2015), State Statistical Office (SSO), Republic of Macedonia
2. Feasibility study and cost benefit analysis for wastewater collection investment projects in the municipality of Kičevo (2015) Safege, Belgrade
3. WWTP outline design, for projects in the municipality of Kičevo (2015) Safege, Belgrade
4. Directive 83/477/EEC (1983) on the protection of workers from the risks related to exposure to asbestos at work, OJ L 263, 24.9.1983, p. 25–32
5. Directive 91/271/EEC (1991) concerning urban waste-water treatment, OJ L 135, 30.5.1991, p. 40–52
6. Directive 2000/60/EC (2000) of the European Parliament and of the Council establishing a framework for Community action in the field of water policy, OJ L 327, 22.12.2000, p. 1–73
7. Main collector detailed design for projects in the municipality of Kičevo, 2015, Safege, Belgrade

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CLASSIFICATION OF ANTHROPOGENIC SEDIMENTS IN ORDER TO WATER PROTECTION IN SERBIA

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ABSTRACT

Humans and its activities have a mainly negative impact on natural processes, as it is in the case of erosion, where humans contributes to the increase of sediment yield. Anthropogenic sediment has not been yet classified and separated from the total amount of sediment. The subject of this paper is separation of anthropogenic sediments from the total sediments. Sediments will be first separated in a certain classes, in regards to sediments sources. Second, the impact estimation and the estimation of sediment quantity of these classes and its effects on the watercourses will be discussed.

Key words: anthropogenic sediments, classification, estimation, water protection.

INTRODUCTION

It is common understanding that erosion and sediment transport are natural phenomenon, which is only partially true. Humans with their actions can significantly change the intensity of erosion and thus the quantity of produced and transported sediments.

During the time it was noted that the amount of sediments produced by human activity is increasing. First were observed sediments type that are visible and recognizable, it is about a surface sediments. The surface sediments is not a new class, long before humans, leaves, branches and trees floated on water, but it was not worryingly because it is a natural biodegradable materials. The problem arose when it suddenly increased the proportion of plastic and other (construction, agriculture, etc.) materials and substances, which became introduced in watercourses from unregulated landfills along the coast and from the hydrographic basin network.

Increased amounts of sediment in rivers threaten a number of important water management objects that rapidly lost their function (river regulation, waterways, reservoirs, canals, etc.), sediment also inflicts a negative effect on the chemical composition of water.

Proportion of these types of sediment is increasing and it is necessary to clearly allocate, because until now these types of sediment were classified as a sediment from natural source. This is necessary for the registration of existing and potential sources of this type of sediment and for finding solutions to reduce its rate in the total amount of sediment.

SEDIMENTS FROM ANTHROPOGENIC SOURCE

All sediment that comes from anthropogenic activities, is anthropogenic sediment. That sediment can be composed of synthetic, natural and mixed materials. Floating artificial materials are first identified and isolated as the sediment of anthropogenic source. It is about a nondegradable PET packaging, and other floating plastic materials. Reason why there are so many garbage in watercourses are unregulated and unprotected garbage dumps, which are mainly found on the banks of rivers and small streams.

The way of movement of surface floating sediment is different compared to other types of anthropogenic sediment that can successfully hide in naturally generated sediment. Visibility of these types of sediment creates the impression that its volumes is significantly higher compared to the other types of natural and anthropogenic sediment due to the large volume in relation to weight. Proportion of surface floating sediment in total sediment is not dominant, but its impact on the ecological status of water and a negative impact on the operation of water management facilities and electric power facilities caused a need to pay a special attention to this type of sediment.

Figure 1. Surface floating sediment that reached the dam on the Tisa river

CLASSIFICATION OF SEDIMENTS FROM ANTHROPOGENIC SOURCE

This paper focuses on the analysis of anthropogenic sediments which is identified with those of natural source, because it has a similar composition and way of movement.

Anthropogenic sediments can be divided into several classes according to their source. The following characteristic classes have been identified:

1. Sediment from gravel dumps, sand and other materials on the shores and in the beds of rivers and streams
2. Sediment from unregulated and unprotected road network
3. Sediment from forests exploiting
4. Sediment source from landslides
5. Sediment from agriculture and fruit production
6. Sediment from industrial and mining waste dumps

These classes are the ones that have been identified in this analysis, and this does not mean that there are no more classes of anthropogenic sediment.

Sediment from gravel dumps, sand and other materials on the shores and in the beds of rivers and streams

River valleys are generally suitable for transport, by water or by land, therefore numerous warehouses are located along the river.

Large sand and gravel dumps and other construction materials, facilities and warehouses are located along the major rivers and in riverbeds for the big water, where are very endangered in the case of flood. Reason for choosing this locations is because that is the easiest way to transfer material from the transport vessel to shore and conversely. Besides the facilities for the separation of sand and gravel there are also warehouses of building materials (cement, lime, timber, etc.), as well as warehouses of agrochemical substances (fertilizers, herbicides and other substances).

The impact of this group of anthropogenic sediment on the environment and ecological status of water is reflected in the chemical composition and increasing the amount of sediment compared to the naturally generated sediment.

Sediment from unregulated and unprotected road network

Sediment from the road network is one of the most common. It is about the sediment generated from roads that was built careless and on people own initiative. Field and forest roads are the biggest problem because people are building theme for accessibility to their crop fields or to their private forests.

The main criteria is unchanged for millennia, and that is that the ups and downs along the road are within the limits that animals can overcome when carrying cargo. Rule that has also remained unchanged is that the route of the roads go by watersheds and along rivers and creeks. Every incautiously turn of the pathway gives rise to increased erosion and rapidly spread of gullies. When this happens the road route in most cases only bypass the situation without remediation the resulting phenomena.

Negative impact of this class of sediment is reflected in increasing volumes of sterile sediments in watercourses.

Sediment from forests exploiting

Forest exploitation is the oldest cause of anthropogenic erosion and sediment. Serbia is no exception to this phenomenon, which has turned a large forested areas in the rocky and sandy deserts in the past. Excessive exploitation of forests in Serbia, since the end of the 19th century to the 50s of the 20th century, has caused unimaginable increase of erosion processes and torrent floods.

Even today everywhere are signs of forest exploitation on steep slopes which does not consider the fact that it is about the forests on the ground that is highly vulnerable to erosion. Figure 8 shows the bottom of the gully with high steep slopes and large longitudinal fall. After cutting numerous trees were fell to the bottom of the gully, and some were fell over the gully. These trees remain in the gully because their extraction is difficult. The weight of these trees can hardly damage the bed of gullies and together with initiated sediment can damage the erodible soil of the gullies bed and thus increase the total amount of sediment load.

Figure 8. Gully along which there are the remains of fallen trees

Sediment source from landslides

Landslides are frequent occurrence in Serbia, and a source of significant amounts of sediments that enters the drainage network.

Human-induced landslides may result from changes in slope caused by terracing for agriculture, cut-and-fill construction for highways, construction activity, mining operations, rapid draw-down of dams, changes in land cover such as deforestation, and changes in irrigation or surface runoff [2].

The human-induced landslides are caused by changes of the strength or effective stresses, changes in geometry and boundary conditions, and modifications or changes of the material behaviour. The most common anthropogenic factor leading to slope instability is the modification of slope profile, usually caused by cut-and-fills that decrease the factor of safety [2].

Sediment from agriculture and fruit production

Anthropogenic impact on the amount of sediment originating from agriculture and fruit production is significant, the wrong way of soil tillage and the wrong choice of culture intensifies erosion. Main reasons are that the agricultural parcels in Serbia are divided along the slopes and tillage is processed down the slope instead along the contour lines.

Arable land and orchards are also a source of pollution that sediment brings along into watercourses. Agrochemical substances (fertilizers and expensive poison weed control and plant protection products), which are used in agricultural production, can get into the sediment and also into watercourses. Therefore, the concern about anthropogenic sediment from agriculture at the same time cares about improving the ecological status of watercourses.

Sediment from industrial and mining waste dumps

Industry and mining in their production process often produces three types of dumps, raw materials dumps, production and mullock dumps. These are natural materials sand, gravel, stone, soil, ores, etc. These materials are in an open area exposed to atmospheric influences. The main problem of these dumps, when it comes to the formation of anthropogenic sediment, is that they have no natural resistance to erosion, so they are easy transported by water or wind.

Unlike mentioned, flotation and ash dumps have a dam that prevents materials from these dumps to reach watercourses, but unfortunately that happens occasionally. In case that this material reach watercourses, it will cause an ecological disaster, because these materials contain elements from the classes of dangerous, harmful and toxic substances.

Application of industrial and mining waste dumps is in the first place threat to the ecological status of surface water and groundwater.

CONTENT ESTIMATION OF ANTHROPOGENIC SEDIMENTS CLASSES IN TOTAL SEDIMENTS

Until the development of procedures for registration the sources of anthropogenic sediment and its quantification, the total amount and its content in total sediment are at the level of estimation.

Based on detailed research into the state of erosion and torrential processes, which has been done over the last decade, it is estimated that anthropogenic sediment in total sediment has a share of 15-20 %, i.e. from 90 to 120 m^3 / km^2 per year. Which means that in Serbia annual average anthropogenic sediment load is 9-10 million m^3.

The share of each of the identified classes of anthropogenic sediment in total sediments is different. The estimation for each class is made and result is given in the following order:

1. Sediment from unregulated and unprotected road network
2. Sediment source from landslides
3. Sediment from forests exploiting
4. Sediment from industrial and mining waste dumps
5. Sediment from agriculture and fruit production
6. Sediment from gravel dumps, sand and other materials on the shores and in the beds of rivers and streams

IMPACT ESTIMATION OF ANTHROPOGENIC SEDIMENTS CLASSES ON WATER ECOLOGICAL STATUS

As well as in the case of the amount of anthropogenic sediment, its impact on the ecological status of the water is also at the level of estimation. Negative impacts estimation of each of the classes on the ecological status of water is given in the following order:

1. Sediment from industrial and mining waste dumps
2. Sediment from agriculture and fruit production
3. Sediment from gravel dumps, sand and other materials on the shores and in the beds of rivers and streams
4. Sediment from unregulated and unprotected road network
5. Sediment source from landslides
6. Sediment from forests exploiting

CONCLUSION

Sediment from anthropogenic source is a phenomenon which is becoming an increasing problem. This paper points out the set of problems and gives a proposal for anthropogenic sediment classification and quantification and impacts estimation.

This type of sediment has two main impacts on watercourses:

1. Increasing the amount of sediment compared to the naturally produced and disrupts the natural balance of erosion and sediment transport.
2. Pollution - certain classes of anthropogenic sediment are specific because they can be harmful, poor in nutrients and contaminated with toxic materials.

For reducing these negative impacts of anthropogenic sediment on the ecological status of water and nature, not require immeasurable large funds and inaccessible technology. Investments are needed only in the case of need to prevent harmful effects of sediment on the environment.

First step is to develop procedures for the registration the sources of the listed classes and their quantification. Each of these sources is the result of human activities so it is necessary to develop procedures for reducing the rate of this sources, or to introduce and implement specific policies and measures.

These two proposals in combination with education of the population, especially kids, would also help with this, in most cases hidden, ecological problem.

REFERENCES

1. Studije ekološkog uticaja antropogenim delovanjem generisanog nanosa na status voda u Srbiji, Institut za vodoprivredu Jaroslav Cerni, Београд, 2012.
2. SafeLand, Living with landslide risk in Europe: Assessment, effects of global change, and risk management strategies, 7th Framework Programme, Cooperation Theme 6 Environment (including climate change), Sub-Activity 6.1.3 Natural Hazards, Deliverable D1.6, Analysis of landslides triggered by anthropogenic factors in Europe, Work Package 1.4 - Landslides triggered by anthropogenic factors, February 2011.

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HEAVY METALS IN SOIL IN SREM (VOJVODINA): CONTAMINATION LEVEL AND MOBILITY

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ABSTRACT

Potentially harmful trace elements pollution in soils is a worldwide environmental problem that has received increasing attention over the last few decades because of its adverse effects. Metals in soils are present in different chemical forms which affect their ability to transfer. The objective of this body of work was to assessment of contamination degree of elements Cu, Hg, Ni, Cr, Co, Zn, Pb, Cd As and B in agricultural and grazing soils surrounding the industrial objects, in order to quantify their real influence and real health risk by using investigated soils as croplands. Combination of different methods was applied for estimation of the environmental status of soils and to determine the potential risk of ecological damage. Obtained results indicate that heavy metal contamination should be taken into account during development of management strategies to protect the soil in the Serbia.

Key words: heavy metals, B, soils, contamination level, mobility factor.

INTRODUCTION

Detailed investigation of heavy metals soil contamination as potentially toxic elements is particularly important, since Serbia has involved recently in systematic examination and assessment of the potential risk and contamination level. This assessment in the area such as Srem and Vojvodina is important considering that the most part is used for agricultural activities. However, in the last century, many industrial objects (especially food industry) were built in this area, reducing the surface of the agricultural area and increasing contamination level. Industrial pollution typically contaminate shallow layers of soil(0-40 cm), and in the case of natural enrichment contamination is present in deeper layers as well (6) The accumulation of heavy metals in soils is a potential risk to human health, firstly because of elements transfer in an aqueous medium, and secondly their adoption by the plant and entering in the food chain.

Many authors studied heavy metals concentrations in agricultural and nonagricultural soils of Vojvodina, and concluded that the value of elements such as Pb, Ni, As, Cd, Cu, Cr mostly were below the maximum allowed concentrations (MAC). However, in the vineyard soils have been identified presence of higher level of Cu, as a result of usage Cu-compounds based fungicides (10). Furthermore, higher nickel content (of geochemical origin) was detected (2,3). In some parts less terraces of Srem, higher values of Ni, Cr, Pb above the MAC in top soils presented as anthropogenic, but in bottom soil as natural (5). Not many authors determined bioavailability of the studied elements. Ni was found as slightly mobile in some parts of Srem (3). Also, Maksimović et al (8) determined low mobility in case of Ni, As, Cu, but in mobile forms are Cd and Pb.

In this paper, the main goal is assessment of contamination degree of elements Cu, Hg, Ni, Cr, Co, Zn, Pb, Cd As and B in agricultural and grazing soils surrounding the industrial objects, in order to quantify their real influence and real health risk by using investigated soils as croplands. Additionally, it is very important to determine how many percents of the measured concentrations are really bioavailable and can undergo the bio-cycle. Thus is possible to evaluate the potential use of the soils in this part of Srem in the future.

MATERIAL AND METHOD OF WORK

Investigated area included 8 towns and different industrial objects: 1.Šimanovci - samples labeled as S1-S5 (metal cutting and boiler factory-S1, printing shop-S2,S3, pesticide factory-S4,S5);2. Pećinci, S6-S8 (sugar factory); 3.Stara Pazova- samples S6-S14 (salt processing plant-S9, printing shop-S10,solid metal waste - S11, metal processing plant (abandoned)-S11-S14); 4.Inđija- S15-S20 (tobacco factory-S15, S16, paint and varnish factory and battery factory-S17, S18, pet food industry and metal factory- S19;sample S20 islocated between these factories); 5. Ruma-S21-26 (leather industry S21, S22 and tire factory S23- S26); 6.Sremska Mitrovica- samples S27-S32 (wood, cellulose and paper factory S27, S28; S29 is placed further, in urban area and sugar mill plant S30-S32);7. Šid samples S33-S41(paint and varnish factory S33-S35,insulation material factory S36, S37 and S38 between this factory and oil mill plant, S41, print shop- S39, S40);8. Beočin –samples S42-S45 (cement factory)

Soil samples were collected in October 2010 at 45 localities around the industrial objects. T he samples were collected with stainless steel shovels on two depths: 10-30 cm and 30-50 cm or 0-10 cm and 10-50 cm depending on type of soils-agricultural or grazing. Sampling methodology defined in the GEMAS project (Geological Mapping of Agricultural and Grazing Soils).

In order to determine distribution – geochemical affinity of metals and their bioavailability modified Tessier sequential extraction (14) were used and included five phases: F1-exchangeable (1MNH_4CH_3COO); F2-metal bound to carbonate sand easily reducible species (0.01M HCl and 0.1M NH_2OH HCl); F3-metal bound to moderately reducible phases or Fe-oxides fraction (0.2M $H_2C_2O_4$ and 0.2M $(NH_4)_2C_2O_4$);F4-organic matter and sulfides (30% H_2O_2 adjusted to pH 2 with HNO_3/ followed by extraction with 3.2M $CH_3COO(NH_4)$; F5-Residual fraction (6M HCl).

Determination of concentrations Cu, Cd, Pb, Cr, Cu, Co, Ni, Pb, B, As, were performed by ICP/AES –(inductively coupled plasma atomic emission spectrometry-iCAP-6500 Duo ,Thermo Scientific, UK). Hg were detected by hydride generation system AAS (atomic apsorption spectrometry (PERKINELMER 6500, MHS-15).

The X-ray powder diffraction (XRPD) studies were performed by automatically diffractometer for powder "PHILIPS", model PW-1710. There was used long-focus (LFF) Cu-anode (U = 40 kV and I = 30 mA), with the monochromatic $K\alpha_1$ radiation (wave-length $\lambda = 1.54051$Å) and Xe proportional counter.

Descriptive statistics, Kolmogorov-Smirnov test for the normality of distribution, Wilcoxon Signed-Rank test were performed using the demo version of NCSS statistical software.

RESULTS AND DISCUSSION

XRD analyses of fraction <0,063 mm showed mineralogical composition: the most dominant mineral is quartz as a primal mineral (with exception of the sample S41, where is dominant calcite),feldspar and clay minerals type illite, sericite, chlorite and montmorillonite. Carbonates - calcite and dolomite are present in different concentration range. In bottom soils, these minerals in some samples are detected in higher percents than feldspar or clays. amphiboles and hematite are detected in soils as well.

The results of heavy metal concentrations as mean, maximum, minimum as well as standard deviations (st. d), are given in Table 1.

Table 1. Descriptive statistic of heavy metal concentrations (mg/kg)

	As	B$^{\#}$	Cd	Cr	Cu	Ni	Pb	Co	Zn	Hg
Mean	6.55	8.50	0.36	49.3	27.9	51.6	21.6	10.7	65.9	0.37
St.d	3.78	4.44	0.17	39.0	15.5	40.4	13.9	3.99	36.7	0.27
Med	6.52	8.03	0.33	36.8	22.8	39.9	18.6	9.97	51.29	0.25
Min	1.09	1.43	0.21	21.1	13.6	23.5	6.42	5.31	33.4	0.07
Max	21.4	24.5	1.27	247	94.4	230	67.7	24.1	192	0.95
Mean	6.48	6.32	0.28	44.8	37.0	49.7	18.2	10.1	55.6	0.23
St.d	3.16	2.74	0.10	29.1	79.6	44.8	15.6	3.55	24.0	0.12
Med	6.77	6.01	0.28	36.9	22.0	36.4	13.5	9.45	52.5	0.22
Min	0.40	0.78	0.16	20.1	14.2	21.7	5.34	5.44	27.4	0.05
Max	12.6	12.8	0.68	152	553	273	95.4	20.2	154	0.57
*mac	20	50	0.6	64	22	17	61.6	4	78	0.15
**iv	37	-	8.4	242	116	101	384	104	400	7.67

*mac-maximum allowed concentration of elements (modified) (Official Gazette of the Republic Serbia, 88/2010) and B$^{\#}$ (Official Gazette of Serbia 23, 1994)

**iv-intervention values (modified)

The main contamination assessment criteria - maximum allowed concentrations (MAC) and intervention values (IV) of metals in soils defined in standard Official Gazette of the Republic Serbia, 88/2010) and for boron- Official Gazette of Serbia 23, 1994 (Table 1) are used. As proposition of standard MAC and IV need to be modified regardless quantity of clay (%) and organic matter (%).The mean of clay and organic matter in the investigated soils are 6,84% and 4,78%, respectively.

Using Wilcoxon's test was found that the contents of B, Cd, Ni, Pb, Zn and Hg are higher in the top soils, i.e.more concentrated in the surface layer. In contrast, copper is more concentrated in the bottom soils.

In accordance with the fact that the distribution of the result does not belong to the normal Gauss distribution, median value compared with the standard values (Table 1). It can be concluded that median values of Ni, Co and Hg exceeds the standard values in both depths and the value of Cu at the surface exceeds but in the subsurface is equivalent to the standard value. Median of concentrations of the other elements do not exceed the MAC (Table 1).

Range of concentrations of nickel indicates that all values in the examined area are above value of 17 mg/kg. The maximum value is registered in both depths of sample taken away 400 m from the cement factory in urban area of Beočin (S43) and nearby the cement factory S42-top soil (106 mg/kg). High values were also detected at the locality S22 (167 mg/kg , top soil), 250 m away from the leather factory and S21 (158 and 148 mg/kg), nearby the factory, in urban area of Ruma town. The range values of chromium content in the investigated area are both below and above limited. The peaks were observed in samples S21 (top soil) and S43 (bottom soil). As mentioned above, some authors concluded that the main origin of Ni in soils and sediments of Vojvodina is geochemical (3,14). The minerals chlorite and amphibole, both detected in these samples can be one of the main source of Ni and Cr (14).These minerals also may be significant sources of Ni and Cr in presented samples as well. The other might be cement factory because of cement- arrived fugitive dust or combustion of fossil fuel. Fugitive dust can be the source of Pb, Zn, Cd, Hg and Cu as well (1,6). In the leather industry are used chromium salts, so it can be one of the sources in this sample (4).On the other hand, combustion of fossil fuel (coil) can be the source of fly ash rich with As, Cd, Pb, Cu, Ni, Co, Mn, Fe, Zn, Cr, B, Hg (6,9) The values of cobalt content are above MAC in the whole researched area, and the maximum value was observed in samples S42 (top soil)and S12 (bottom soil), placed near metal processing plant. According to the concentration range of copper, it can be concluded that there are soils with copper content below and above MAC. The maximum values were recorded again 400m from cement factory (S43) and the extremely high value of copper detected in sample taken 250 m away from the leather factory, in an abandoned orchard and probably originates from the usage of copper-based fungicides Bordeaux mixture type, used earlier, much before the sampling. Here should be noted that these fungicides can contain lead and zinc as well (11). The value range of content Hg, indicates variety of concentration distribution in the soil around the industrial facilities. The highest values are registered in the sample (both top soil): S21 and S27-sample of agricultural soil, taken nearby cellulose factory and S7 (bottom soil), taken 400 m away from the sugar factory in Pećinci town. Most probably presence of Hg in soils is a consequence of fossil fuels combustion and agrochemicals usage. Concentration of Pb in soils around industrial facilities are below the MAC according to given standards. The exceptions are the max value in the sample S42 (top soil, Table 1). Also, higher value are registered in the sample S29 (65.3 and 95.4 mg/kg) in an urban area of Sremska Mitrovica town, taken

250m away from the wood and cellulose factory and sample S-28 (54,6mg/kg topsoil), 400m further. The origin of lead thus could be usage of fertilizers, pesticides, fuel combustion or cement fugitive dust and urban area activities. Popović et al (13) explained unexpected value of lead in the soil placed further from heavy traffic as mixture of influences: cement factory in Beočin and traffic. Maximum values of zinc detected in samples S21 and S12 (top soil and bottom soil, respectively). Metal processing factory can be a source of metal Cr, Ni, Fe, Zn, and Cu (12), Values of Cd content in the soils of studied area are both higher and lower than the limited value. The highest concentration was detected at locality labeled S4-sample of agricultural soil, placed between pesticides factory and building material factory in Šimanovci town, as well as in the sample S42 (topsoil (0.63mg/kg).The origin of Cd can be agricultural activities, and fossil fuel combustion, since that presence of Cd, and Pb detected in fertilizers which have been used in Serbia (15). Arsenic content in all samples is below MAC, except sample S41, where is registered the maximum value (Table 1). The contents of boron in all samples are below the MAC of 50 mg/kg. The maximum was recorded in the sample S-11(agricultural soil) next to solid metal waste in Stara Pazova town, probably as the result of using fertilizers.

As summary, the most contaminated samples are: S12 contaminated with Ni, Co, Cr, Zn, Cu; S21- Ni, Cr, Hg, Cu, Zn; S 22- Ni, Cu ,Cr, Hg, Zn; S29- Pb, Zn,Ni, Cu, Cr,Hg; S42-Ni, Cu,Zn,Hg; S43-Ni, Cu, Cr,Hg. Obviously, the greatest influence on investigated area soils can have factories: cement and leather factory, metal processing factory and besides that urban activities and usage of agrochemicals.

Geochemical affinity and distribution of the elements between phases F1-F5 is present in Diagram (Figure 1).The elements: Zn, As, Pb, Cr, Ni, Co, B, and Cu are mostly concentrated in residual fraction (F5). The exception is Cd in top soils (dominant presence in carbonate phase -F2), and Hg (dominant presence in exchangeable phase - F1). This distribution of the elements suggest both, the natural and anthropogenic origin. In order to assess the potential mobility and bioavailability of metals, as well as environmental and health risk, the distribution of element concentration between phases is used to calculate mobility factor (MF). MF is calculated as a ratio of soluble, exchangeable and carbonate-bound fraction (in our case F1 and F2), and sum for all fractions (%)(7)

The results of mobility factor (MF) for both depths, (presented in Diagram - Figure 2), pointed the most higher values in case of B (52.82 and 56.73%), Hg (56.64 and 45,17%) and Cd (42.19 and 34.12%). MF values of the other elements decreases: As>Co>Pb>Ni>Zn>Cu>Cr in top soils and Co>As>Pb>Ni>Cu>Zn>Cr in bottom soil. The obtained results indicate that if there was changing in pH value or increasing the ion activity/concentration in soil solution, it would change balance and the elements become mobile in specified percentages.

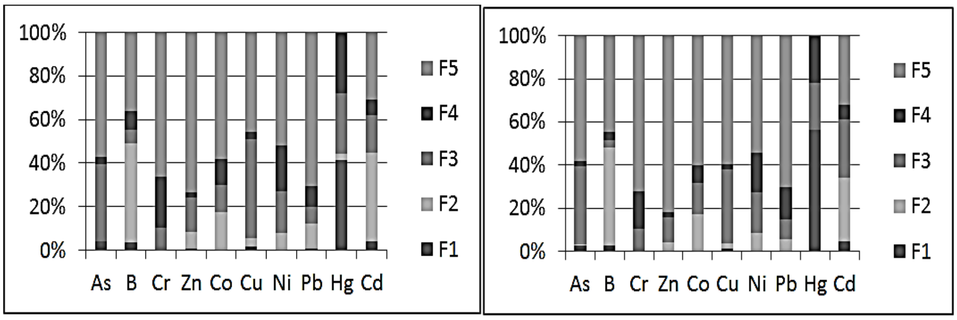

Figure 1. Diagrams of distribution elements between phases (F1-F5) in top soil and bottom soil

Furthermore, MF factor indicates that in case of Cr there is no risk to become mobile and bioavailable (Cr<1%), since it is mostly distributed in low-mobility fractions. There is low risk for Cu, Ni, Zn (1-10%), medium risk for Pb, Co and As (10-30%), high risk for Cd and Hg (top soil), and very high risk for B and Hg(bottom soil, above 50%).

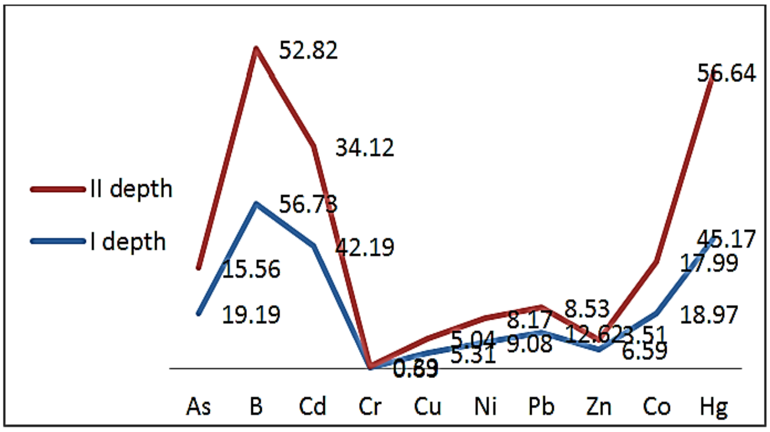

Figure 2. Mobility factor (%) of the elements in top and bottom soils

Accordingly discussion above, it is possible to conclude for the group of elements which mean values or median (Table 1) exceeds MAC, such as Ni and Co, do not have significant environmental influence to, since they are distributed mostly in less mobile forms. This indicates their dominate geochemical origin. In contrast, mean values and median of cadmium and boron are below the limit, but in the soils of research area of Srem, this element can easily become mobile, since bounded in carbonate/slightly reducible phase. Hg is toxic element of very high potential risk, and it indicates anthropogenic influence.

CONCLUSION

Comparing the median values of toxic elements of soils surrounding the industrial objects to the defined standard is obvious that concentrations of Ni, Co, Hg, and Cu in the top and bottom soils are higher, but below the intervention values. Also, B, Cd, Ni, Pb, Zn and Hg, are more concentrate in top soils, and Cu in bottom soils.

Accordingly these criteria, the most contaminated area is Beočin, because of the increased content of Cr, Ni, Cu, and Co which can be influenced firstly of geological matrix (the presence of ultramafic and mafic rocks) and secondly presence of cement factory which could attribut increasing of As, Pb and Cd. Higher values of toxic elements in the investigated area could be consequence of presence of the other industrial objects and combustion of fossil fuel in industrial processes, usage of fertilizers and pesticides, fungicides and activity in urban area .Hg, Cd and B are the most mobile elements in studied sediments and Cr is the least bioavailable, which suggests it′s geochemical origin.

The results of this investigation suggest existence of localities with high level content of toxic metals, but there is evidence of lower level of mobility and bioavailability, except Hg in some localities. Thus, some parts of investigated area can be used as agricultural, but with constant monitoring of contamination level.

REFERENCES

1. Banat K.M. (2005) Heavy metals in urban soils of central Jordan: Should be worry about their environmental risks?, Environmental research 97, 258-273
2. Brankov M. (2006) Trace elements and heavy metal contents of agricultural and nonagricultural soils in the region of Banat, Proceedings 42, 169-177, Institute of field and vegetable crops, Novi Sad
3. Dozet D (2011) Origin and content of Ni in alluvial-delluvial soils of Srem, Serbia, Field and vegetable crops research 48, 369-374
4. Gitet H. (2013) Speciation to chromium in soils near Sheeba leather industry, Wukro Ethiopia, Talanta 116, 626-629
5. Jakšić et al, (2012) Content of Heavy Metals in gleyic chernozem of Srem loess terrace under Alfalfa, Field and vegetable crops research 49(2), 189-194
6. Krishna A.K. (2007) Soil contamination due to heavy metals from an industrial area of Surat, Gujarat, Western India, Environmental monitoring assessment 124, 263-275
7. Mahanta (2009) Total concentration, fractionation, mobylity of heavy.metals in soils of urban area of Guwahanti, India, Environment monitoring assessment, 173,221-240
8. Maksimović L. (2012) Soil contamination in South Backa Region of Serbia with dangerous and harmful substances, Field and vegetable crops research 49(2) 220-228
9. Nable R.O (1997) Boron toxicity, Plant and soil 193, Kluwer Academic Publishers 1997, Netherlands, pp 181-198

10. Ninkov J. (2010) Heavy metals in vineyard soils of Vojvodina province, Field and vegetable crops research 47(1), 273-279
11. Orešković S. (2011) Bordeaux mixture-a comparative investigation of different formulation, Pesticide and Phytomedicine, 20, 255-259
12. Panagopoulos I.(2015) Investigations of potential soil contamination with Cr and Ni in four metal finishing facilities at Asopos industrial area, Journal of hazardous materials 281, 20-25
13. Popović V. (2008) Distribution and accumulation of Pb in soils and wheat, 2nd joint PSU-UNS International conference in bioscience: food, agriculture, environment. Proceedings, 292-296, Novi Sad
14. Sakan S. (2010) Trace element as tracers of environmental pollution in the canal sediments (alluvial formation of the Danube river, Serbia) Environmental monitoring assessment 167, 219-233
15. Zeremski-Škorić T. (2015) Heavy metal content in some fertilizers used in Serbia, Field and vegetable crops research 47(1), 281-287

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POSSIBILITY OF REMOVING LINDANE FROM WATER USING FERRATE(VI)

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ABSTRACT

In order to remove Lindane from water different amounts of ferrate(VI) were added to the solution. Concetration of lindane has kept constant at 10 µg dm^{-3}, while concentration of ferrate(VI) ranged from 10 mg dm^{-3} to 1000 mg dm^{-3} depending on the sample. The influence of Fe^{3+} ions on removal on lindane has also been investigated. Concentration of iron(III) sulfate also ranged from 10 mg dm^{-3} to 1000 mg dm^{-3} depending on the sample.

Key words: Lindane, insecticide, Ferrate(VI), iron(III) sulfate.

INTRODUCTION

Lindane is organochlorine agricultural insecticide that was used worldwide. It is very persistent compound in the environment that can bioaccumulate in food chain [1, 2]. Chemical formula of lindane is $C_6H_6Cl_6$ also known as *gamma*-hexachlorocyclohexane, (γ-HCCH). Residual amounts of lindane have been found in ground and river water, sediments and plants which increased concern about its use. Long time exposure can damage the nervous system and can cause cancer and some related diseases [4]. Around 20% of lindane evaporates into the atmosphere after the use, from there it can be spread to soil and surface water by rainfall [3]. Large concentrations of lindane in soil and water can be found in India, where it was most used during the past century [2]. In 2009, the production and agricultural use of lindane was banned under the Stockholm Convention on persistent organic pollutants but its long life and resistance to chemical transformations makes it appear even today. Upper limit of lindane in drinkable water, according to Serbian Ordinance on the hygienic quality of drinking water ("Službeni list SRJ", br. 42/98 and 44/99) is 0,02 µg dm^{-3}.

Results presented in this paperwork shows that ferrate(VI) can be used for treatment of drinkable water contemned with lindane.

EXPERIMENTAL

Dipotassium ferrate(VI) solution was electrochemically synthesized by transpassive anodic oxidation of electrical steel in 10 M KOH. This method of synthesis is very similar to method shown in [5]. Solid dipotassium ferrate was obtained from concentrated ferrate solution by crystallization and precipitation on -18°C and then by filtration on sinter-glass filter with B3 porosity. Determination of purity of solid dipotassium ferrate was done by standard chromite method [6] and yielded 93,44%.
Lindane was HPLC grade and was obtained from Uni-Chem. Iron(III) sulfate and n-hexane were obtained from Centrohem.

All solutions were made with three times distilled water.

Two different experiments of four sets per experiment were carried on. The first experiment is about to show the effect of ferrate(VI) on lindane removal, and second experiment shows the effect of iron(III) ions on lindane removal. Ferrate(VI) ions first oxidizes the lindane molecules and then Fe^{3+} ions, which are formed from reduction of ferrate(VI) ions, take part in coagulation process which helps in lindane removal. Oxidation of lindane with ferrate(VI) is showed in equation (1).

$$4C_6H_6Cl_6 + 15FeO_4^{2-} \rightarrow 15Fe^{3+} + 24CO_2 + 12H_2O + 24Cl^- + 51e^- \qquad (1)$$

The second experiment shows the effect of iron(III) ions alone in coagulation process. Iron(III) sulfate (anhydrous) was used in this case because sulfate ions do not interfere.

Stock solution of lindane, from which other solutions were made, was prepared this way: 1 mg of solid lindane was dissolved in 200 ml of n-hexane, then 2 dm^3 of distilled water was added and the solution was left to steer on magnetic steering for 48h on 40 °C with speed of 400-500 rounds/min. Phases (water/hexane) were separated using separation funnel. 200 ml of n-hexane was taken for determination of remaining lindane. Lindane were determined on Agilent 7980A gas chromatograph. Results showed that 0,84 mg of lindane remained in 200 ml of n-hexane, that means that 0,16 mg of lindane dissolved in 2 dm^3 of water. This solution of 0,08 mg/ dm^3 of lindane in water will be *Solution L.*

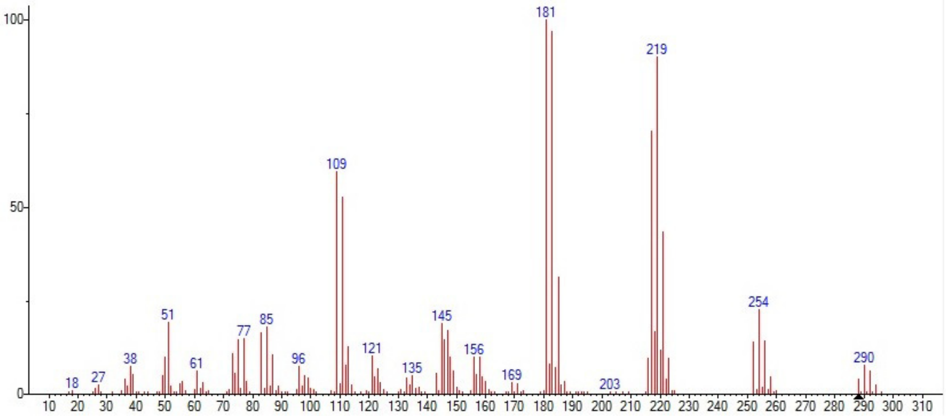

Figure 1. Mass spectrum of lindane from Agilent 7890A GC

In the first experiment in all three sets a 62,5 ml of Solution L is poured in 1000 ml volumetric flask, different amounts of solid K_2FeO_4 per set were added, and filled with water untill 1 dm^3 was reached. Concentration of lindane was the same in all sets 10 $\mu g/dm^3$. Amounts of added dipotassium ferrate(VI) were 10 mg, 50 mg, 100 mg and 1000 mg which is presented in Table 1.

The second experiment was carried out as first experiment which is presented in Table 2.

RESULTS AND DISCUSSION

Every four solutions in the both experiments are left to stay for 72h in dark on 25°C. Then all solutions were filtered on sinter-glass filter with B3 porosity to remove $Fe(OH)_3$. In all samples 200 ml of n-hexane were added to extract remaining lindane.

Table 1. Rection between lindane and ferrate(VI) in water solutions

SET	C_0(Lindane) ($\mu g\ dm^{-3}$)	C_i(Ferrate) ($mg\ dm^{-3}$)	C_r(Lindane) ($\mu g\ dm^{-3}$)
1	10	10	8,21
2	10	50	2,95
3	10	100	0,41
4	10	1000	0,0191

As the concentration of ferrate increases, the concentration of lindane drops. In the very large excess of ferrate it is possible to reduce concentration of lindane to acceptable level.

Table 2. Rection between lindane iron(III) sulfate in water solutions

SET	C_0(Lindane) ($\mu g\ dm^{-3}$)	C_i($Fe_2(SO_4)_3$) ($mg\ dm^{-3}$)	C_r(Lindane) ($\mu g\ dm^{-3}$)
1	10	10	9,33
2	10	50	9,31
3	10	100	8,68
4	10	1000	8,61

From the second set of results we can see that iron(III) ions alone are not effective in removal of lindane from water, but they do contribute, on the small scale, on its concentration.

Initial concentrations of lindane are showed as C_0, C_i are concentrations of K_2SO_4 and $Fe_2(SO_4)_3$ in each set, and C_r is the remaining concentration of lindane after reaction in water solutions.

Results are better presented on the Figure 2. and the Figure 3.

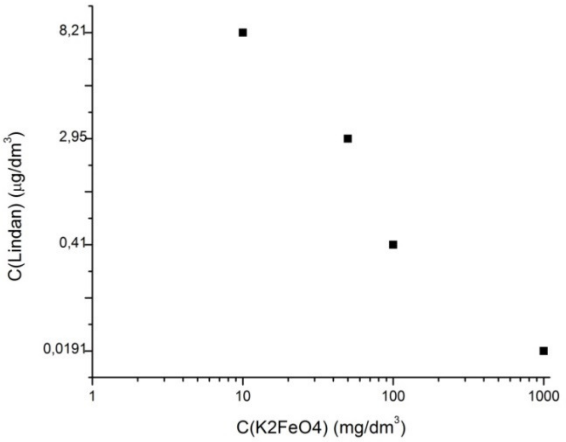

Figure 2. Rection between lindane and ferrate(VI) in water solutions

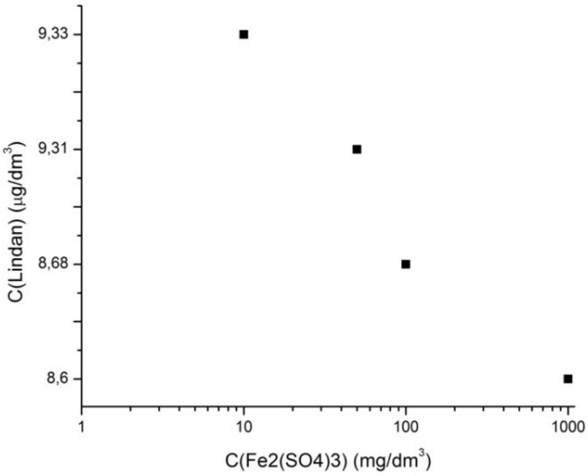

Figure 3. Rection between lindane iron(III) sulfate in water solutions

CONCLUSION

Ferrate(VI) can be used for removal of lindane from water solutions. It offers a very clean and ecologically acceptable solution to treat this pollutant. As mentioned before in the very large excess of ferrate(VI) in the water it is possible to reduce concentration of lindane to acceptable level. In the future, a different kinds of chlorinated organic compounds may appear with the same purpose, and ferrate shows great potential to deal with them.

Acknowlegment

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REFERENCES

1. A. Nienow, J. Bezares-Cruz, I. Poyer, I. Hua, C. Jafvert, Hydrogen peroxide-assisted UV photodegradation of Lindane, Chemosphere 72 (2008) 1700–1705
2. H. Li, G. Sheng, W. Sheng, O. Xu, Uptake of trifluralin and lindane from water by ryegrass, Chemosphere 48 (2002) 335–341
3. A.M. Kipopoulou, A. Zouboulis, C. Samara, Th. Kouimtzis, The fate of lindane in the conventional activated sludge treatment process, Chemosphere 55 (2004) 81–91
4. J. Senthilnathan, L. Philip, Photocatalytic degradation of lindane under UV and visible light using N-doped TiO2, Chemical Engineering Journal 161 (2010) 83–92
5. M.I. Čekerevac, Lj.N. Nikolić-Bujanović, A.B. Jokić, M.V. Simičić, Investigation of electrochemical synthesis of ferrate: Part II Optimization of process parameters and methods of process analytical control , Hem. Ind., 64 (2010) 111-119
6. Z. Luo, M. Strouse, J. Jiang, V. K. Sharma, Methodologies for the analytical determination of ferrate(VI): A Review, Journal of Environmental Science and Health, Part A Toxic/Hazardous Substances and Environmental Engineering, Volume 46, 2011 - Issue 5

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FOOD AVAILABILITY ANALYSIS FOR GRIFFON VULTURE (*Gyps fulvus*) IN CADIZ PROVINCE, SOUTHERN SPAIN

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ABSTRACT

Cadiz Province, Andalusia, has the highest density of breeding Griffon vultures (*Gyps fulvus*) in Spain. Due to changes in carcass removal policy and extensive livestock farming, there is a need for assessing food availability for the species. The amount of dead biomass in wet and dry season was determined by using livestock census data and information from the farmers. Spatial analysis tools were applied for the redistribution of livestock within present land cover classes. The total available biomass significantly differs between seasons, 31%. On average, 56% less of biomass is available in the field than before carcass removal is applied.

Key words: Griffon vulture, Cadiz, land cover, livestock, available biomass.

INTRODUCTION

Griffon vultures, also known as Eurasian griffons (*Gyps fulvus*), are large raptors specialized in the consumption of large carrion. As large scavengers they feed on carcasses of large and medium sized-animals; mostly livestock and wild mammals [1]. They have a sanitizing function in nature as they feed on mammals that died as a cause of various infectious diseases [2]. They had wide distribution ranges over the Western Palearctic [3] and, at present. The largest population in Europe is located in Spain with approximately 25.000 breeding pairs or approximately 80.000 individuals [4]. This species is listed in The IUCN Red List of Threatened Species under the category Least Concern (LC), [5]. They are also protected under international Conventions and Directives: EU Bird Directive, Bern Convention and CITES [3].

Cadiz, a Province in Southern Andalusia and study area of this research, has the highest density of breeding Griffon vultures in Spain. Food availability is the main factor in population regulation of this species [5]. A large percentage of the diet of Griffon vultures in Andalusia in terms of frequency of prey and biomass are cows, horses, goats and sheep [1]. Extensive livestock farming plays an important role in food availability for these birds, therefore the presence of Griffon vultures in Spain is highly dependent on the existence of extensive livestock farming [6]. Cattle's farming is decreasing in Europe and Iberian Peninsula, including Spain, which has a negative consequence on the amount of food availability for raptors [7]. Mosaic land cover types such as grassland, arable land, shrubs, mixture of trees and shrubs with crops or grass and forest are important foraging habitats for these raptors. These land cover types are used in a different way along the year for livestock grazing. At present there is insufficient knowledge about the temporal aspect of livestock distribution within land cover types and also on temporal aspect of livestock mortality rate, which influence the quantity of dead biomass available in different seasons.

The appearance of mad cow disease led to the tightening of the European Union sanitary legislation (Regulation CE 1774/2002) which established limitations on the amount of dead animals left in the field and supplementary feeding stations "vulture restaurants"[8]. However, Regulation (EC) No 1069/2009, as stated in the Commission Regulation (EU) No 142/2011 from 25 February 2011, allows usage of entire bodies or parts of dead animals for the feeding of endangered or protected species of necrophagous birds and other species living in their natural habitat outside feeding stations without prior collection of the dead animals [9].

It is still uncertain how much this legislation has influenced the amount of available biomass in Cadiz. This research will focus on livestock distribution per land cover types along the year. Therefore, variation in livestock mortality rate in both seasons and impact of carcass removal policy on the amount of total dead biomass available for Griffon vultures will also be analyzed.

METHODS AND MATERIALS

For the purpose of primary data collection we performed fieldwork in Cadiz province, the study area, from 3rd to 25th October 2016. Questionnaires were passed among farmers in order to obtain necessary information on livestock: number of dead animals per farm – used for mortality rate calculation; information on grazing areas in wet and dry season – used for analysis of spatial distribution of livestock within land cover classes in both seasons. In order to take samples on the land cover, stratified random sampling technique was applied. As for visiting the farms (77 sampled farms), purposive and random sampling was applied. A set of analysis was carried out to determine food availability analysis for Griffon vultures. Spatial analysis tools were used for mapping the distribution of livestock, carcasses and biomass. Firstly, the land cover map CORINE (250m resolution) was derived from European Environment Agency database [10]. The initial attribute table of CORINE had three levels of classes. Based on sample points on land cover, collected in the field, classes were regrouped to 4th level as follows: built-up, crops, grass, shrubs, forests, mixture of trees and shrubs with crops or grass, olives and other fruits, bare ground, marshes and surface water. Livestock census data was obtained from Department of Agriculture, Fisheries and Rural Development of Cadiz. Data on livestock population (cattle, goats and sheep) within municipalities of

Cadiz, for 2015 and 2016, was used for the analysis. Based on the answers given by the farmers during the fieldwork, certain land cover classes are used for grazing differently in wet and dry season (Figures 1, 2 and 3). The period from January to April, and months November and December was defined as the wet season and the period from May to October is defined as the dry season. The percentage of area used for grazing in wet and dry season was converted into fractions which were applied to livestock census data. Livestock census data was redistributed within land cover per each municipality in wet and dry season. Secondly, the map of carcass distribution in wet and dry season was produced. This was done by the application of a mortality rate to the livestock distribution. The percentage of carcass removal, obtained from questionnaires, was taken into consideration. Out of the total number of sampled cattle farms, 34% dispose carcasses in the field and 66% remove carcasses from the field. Furthermore, out of the total number of sampled goat farms, 48% leave carcasses in the field and 52% remove from the field.

Finally, the biomass distribution maps in the wet and dry season (i.e. total dead biomass of cattle, goats and sheep together) was produced (Figures 4 and 5) by applying formula as shown below:

Total dead biomass distribution within municipalities = Number of carcasses per municipality x average animal weight x percentage available biomass of total animal weight

In order to analyze whether the difference between total amounts of biomass available for Griffon vultures between two seasons is significant, paired 2-sample t-test was carried out at 95% confidence level. Next, the comparison analysis was done between the amount of biomass available for Griffons without carcass removal from the field and the amount of biomass left after carcass removal from the field, by applying paired 2-sample t-test at 95% confidence level.

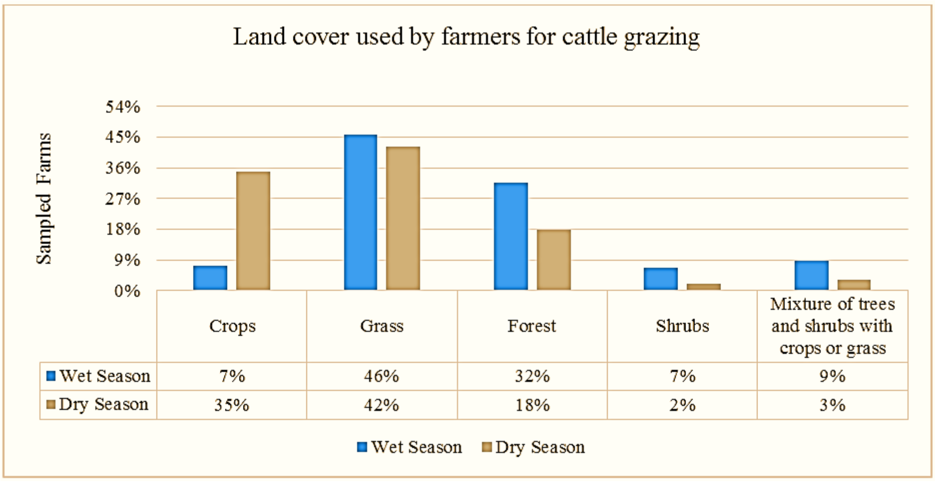

Figure 1. Percentage of land cover used for cattle grazing by farmers in wet and dry season.

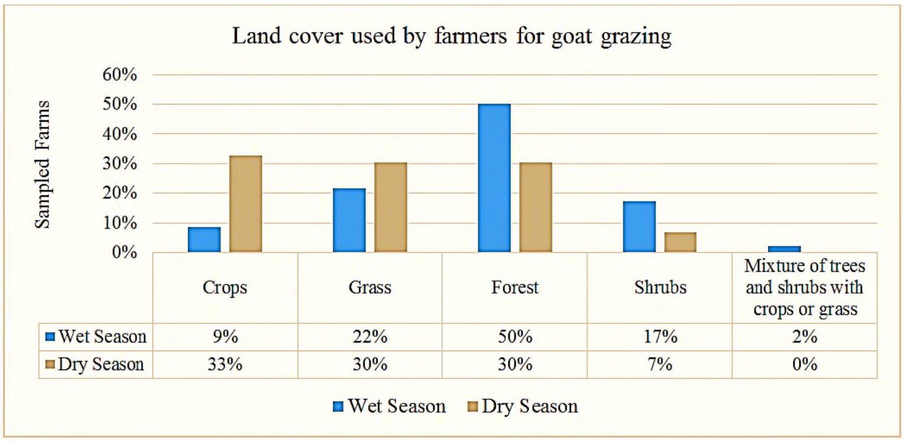

Figure 2. Percentage of land cover used for goat grazing by farmers in wet and dry season.

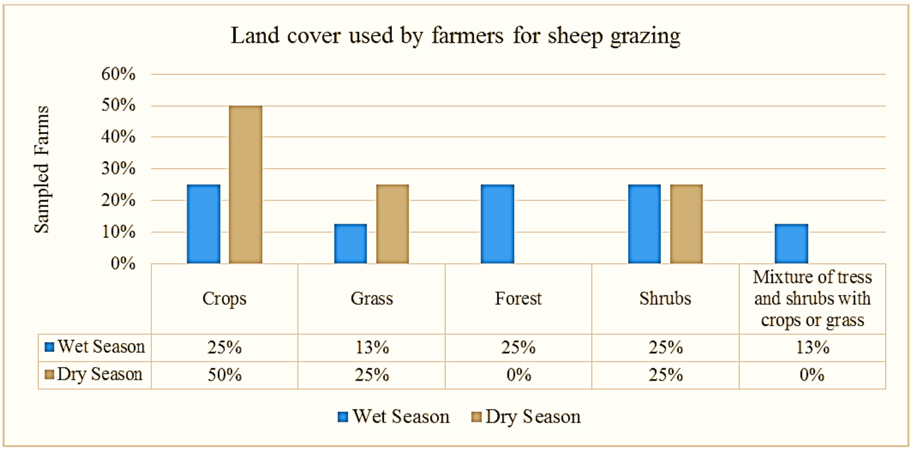

Figure 3. Percentage of land cover used for sheep grazing in wet and dry season.

RESULTS AND DISCUSSION

The final output of food availability analysis have been produced as maps of total dead biomass distribution, both in wet and dry season (Figures 4 and 5). These maps show the amount of dead biomass in kg within municipalities available for Griffon vultures. The amount of biomass does not reflect the amount of carcasses. Griffons are adjusted to feed on soft tissues of dead animals, so bones are not part of their diet. Therefore, only part of total carcass biomass, without bones, is considered in the research.

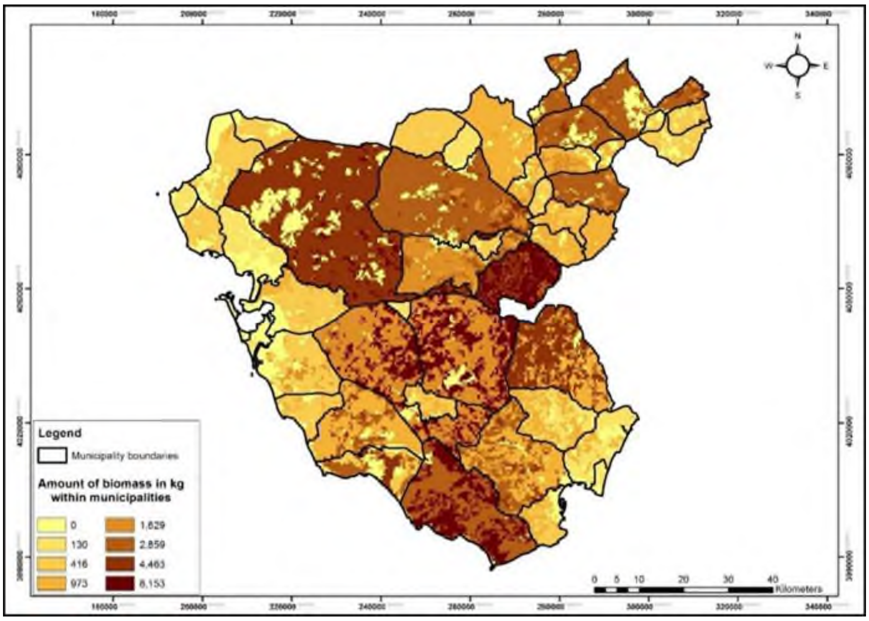

Figure 4. Amount of dead biomass in kg within municipalities available in wet season.

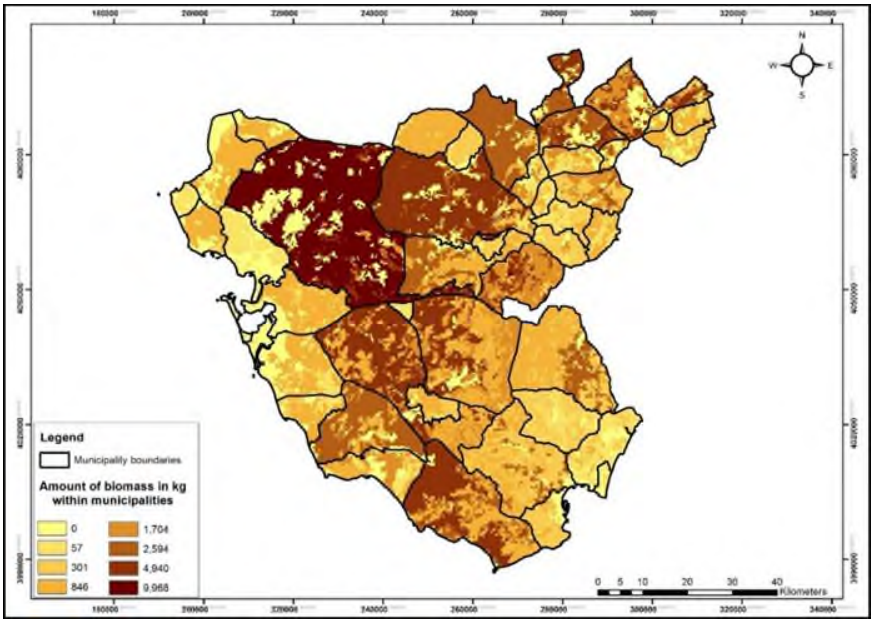

Figure 5. Amount of dead biomass in kg within municipalities available in dry season.

The results of paired 2-sample t test showed that there is a significant difference between the total available dead biomass in wet and dry season ($P < 0.001$), after carcass removal from the field. There is 31% less biomass available for Griffon vultures in dry season as compared to wet season. Difference in the total available biomass between wet and dry season could be the result of the seasonal difference in the number of livestock present within certain land cover types and because of this the seasonal difference in mortality rate of livestock. Forests and shrub lands that cover mostly eastern and southern parts of the Province, are highly suitable for goats and sheep grazing. Number of dead goats in wet season is notably higher than in dry season. By considering these factors, it is clear why there are more carcasses, and therefore dead biomass, in this part of study area in wet season. In northern parts of Cadiz Province where crops occupy a large surface there are more available carcasses in dry season. This is due to the fact that area covered by crops is used for cattle, goats and sheep grazing more during this period of the year (harvesting period), and thus more available carcasses are expected.

Furthermore, the results showed that there is a significant difference in the total amount of dead biomass available in the field before and after carcass removal, applied by farmers ($P = 0.04$). On average, 56% less of biomass is available in the field than before carcass removal from the field is applied. So carcass removal policy showed to be an important factor in the amount of dead biomass available in the field for Griffon vultures.

CONCLUSION

Extensive livestock farming is a significant activity influencing food availability for Griffon vultures. Mosaic of habitats in Cadiz Province, formed by the presence of forest, grasslands, shrubs and crops, are an important factor in extensive livestock grazing. Livestock represent potential food for Griffon vultures, thus its spatial distribution may influence its movement ecology. Seasonal differences in mortality rate of livestock, lead to significant differences in the amount of carcasses available in the field between wet and dry season. Dry season which is characterized with the less amount of food, in comparison to wet season, coincides with a breeding period and it is the period of the year when youngsters need food. Therefore, foraging may be a real challenge in this period of the year.

Many farmers, conditioned by EU sanitary legislations, remove dead animals from the field for industrial disposal which influences the amount of carcasses available for Griffon vultures. During interviews, there were many complaints among farmers on the costs they are forced to spend for the services in order for carcasses to be removed from the field.

A reduction in numbers of supplementary food may trigger significant changes in the diet composition and also in habitat use. Information concerning the maintenance of extensive grazing systems and monitoring the impact of carcass removal policy contributes to decision making for the conservation of Griffon vultures in Cadiz, but also applicable for other areas in Spain or Europe.

REFERENCES

1. Grubac, B. (2014): Gyps fulvus, 12 - 99, Institute for nature conservation in Serbia, Belgrade.
2. Marinkovic, S., Karadzic, B. (2008): Gyps fulvus, 30 - 35, Institute for Biological Research "Sinisa Stankovic", Belgrade.
3. Slotta-Bachmayr, L., Bögel, R., Cardenal, A. (2004): Status report and Action Plan: The Eurasian Griffon vulture (*Gyps fulvus*) in Europe and the Mediterranean , 10 - 12, East European/Mediterranean Griffon Vulture Working Group (EGVWG), Salzburg.
4. Del Moral, J.C. (2009): El buitre leonado en España, Población reproductora en 2008 y método de censo, 170, *SEO/BirdLife*.
5. Parra, J., & Tellería, J. L. (2004): The increase in the Spanish population of Griffon Vulture Gyps Fulvus during 1989–1999: effects of food and nest site availability, Bird Conservation International, 14: 33 - 41, BirdLife International, United Kingdom.
6. Donázar, J. A., Naveso, M. A., Tella, J. L., & Campión, D. (1997): Extensive grazing and raptors in Spain, In D. J. Pain & M. W. Pienkowski (Eds.): Farming and birds in Europe: The common agricultural policy and its implications for bird conservation, Academic Press, 117-149, San Diego.
7. Caballero, R. (2007): High Nature Value (HNV) Grazing Systems in Europe: A Link between Biodiversity and Farm Economics, The Open Agriculture Journal, 1(1), 11–19, Bentham Science Publisher Ltd., United Arab Emirates.
8. Donázar, J. A., Cortés-Avizanda, A., & Carrete, M. (2010): Dietary shifts in two vultures after the demise of supplementary feeding stations: consequences of the EU sanitary legislation, European Journal of Wildlife Research, 56(4), 613–621, Springer-Verlag, Berlin.
9. Regulation (EU) No 142/2011. 2011. Commission regulation (EU) No 142/2011 of 25 Feb 2011 implementing regulation (EC) No 1069/2009 of the European Parliament and of the Council laying down health rules as regards animal by-products and derived products not intended for human consumption, Official Journal of the European Union.
10. Datasets—European Environment Agency (EEA). (2016), http://www.eea.europa.eu/data and maps/data#c17=&c11=&c5=all&c0=5&b_start=0&c12=corine+land+cover+raster+data (accessed February 9, 2017).

GLOBAL AND ENVIRONMENTAL HEALTH – IMPERATIVES FOR THE 21 CENTURY

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ABSTRACT

Introduction: Global and environmental health for all populations have become an accepted international goal. Many factors outside the health system determine individual health and social wellbeing. *Objectives:* to investigate global and international experiences, scenarios and avenues towards the environmental and sustainable health. *Method:* data was gathered through search of PubMed. *Results:* Cited research provides substantial evidence of strong correlation between exposure to environmental hazards and health risks, longevity and health quality, in both developed and developing world and a need for substantial policy interventions. *Conclusion*: Serbia has to establish national health objectives for sustainable health, and strengthen favorable political, economic, environmental, social, cultural and behavioral factors for health, enabling people to take control of factors influencing their environment, health and mediation for multi-sectoral action.

Key words: sustainable health, environment, health objectives.

INTRODUCTION

> "If you want to learn about the health of a population, look at the air they breathe, the water they drink, and the places where they live."
> *Hippocrates, the Father of Medicine, 5th Century BC*

Why is environmental health so important? Most often people think of the environment in terms of the natural environment – soil, water, air, plant and animal wildlife, seasons and the weather. Other definitions of the environment focus on the human-made environment, which includes features such as housing, work, school and child care facilities, transportation, industry and agriculture. Because of its potential to harm human health, concern for the relationship between the natural environment and human health has been a basis of public health practice from late 19 century. In contrast, general public awareness of the environmental issues has developed only in the last several decades. The "environmental movement" introduced into everyday life such terms as "water quality," "clean air," "ozone hole," "urban sprawl," and "soil contamination". The focus of the environmental movement in the seventies was predominantly ecological and concerns were centered on human's negative effects on the nature. Later, this focus has shifted to environmental risks for human health, especially for the children health and, more recently, to risks associated with human-made environments: homes, schools, work places, cities [1].

Imbalances in the world, such as the wealth gap, generational gap, and poverty, have direct negative impact on environment and health. Poor societies have lower availability of healthy food and clean water, fewer doctors and pharmacies, inadequate transportation and recreation facilities. Poverty has a substantial impact on the environment because the poor have less access to services, less formal and informal education and information which is associated with risk behaviors. Permanent people's migration increased risk of communicable diseases. In such a situation it is difficult, if not impossible, to provide quality public health systems [2].

METHOD

Data was gathered through search of free sources, PubMed and National Library of Medicine, and analyzed from the perspective of global and sustainable health.

RESULTS AND DISCUSSION

The environment. The interaction between human health and the environment has been extensively studied and environmental risks have been proven to significantly impact human health (Table 1), either directly by exposing people to harmful agents, or indirectly, by disrupting life-sustaining ecosystems.

Table1. Environmental safety and health hazards

Safety hazards	Result in injuries through the uncontrolled transfer of energy to vulnerable recipients from sources such as electrical, thermal, kinetic, chemical or radiation energy
Health hazards:	Result in environmental or occupational illnesses
- *chemical*	Heavy metals (lead and mercury), pesticides, organic solvents (benzene and trichloroethylene), etc. There are approximately 80,000 chemicals in commercial use, 15,000 of which are frequently produced or used. Approximately 1,000 new chemicals are added to commercial use annually
- *physical*	Excessive noise, vibration, extreme temperatures and pressure, ionizing and nonionizing radiation
- *biomechanical*	Heavy lifting, repetitive, awkward or forceful movements that result in musculoskeletal disorders, like carpal tunnel syndrome and low back pain
- *biological*	Human immunodeficiency virus (HIV), hepatitis B and hepatitis C viruses, the tubercle bacillus, other bacteria, viruses and microorganisms that may be transmitted through air, water, food or direct contact
- *psychosocial*	high stress due to excessive demands on workers on the workplaces, unemployment stress, stress and hostility resulting from urban congestion, etc.

Although the exact contribution of environmental factors to the development of death and disease cannot be precisely determined, the World Health Organization (WHO) has estimated that thirteen million deaths annually are attributable to preventable environmental causes. The report also estimates that 24% of the global disease burden (healthy life years lost) and 23% of all deaths (premature mortality) are attributable to environmental factors, with the environmental burden of diseases being 15 times higher in developing countries than in developed countries, due to differences in exposure to environmental risks and access to health care [3].

Scientists, policymakers, and the public have raised concerns about children's exposure to environmental contaminants such as lead, mercury, and synthetic chemicals like pesticides [4, 5, 6]. There are also significant concerns about possible links between environmental exposures to common chemicals and asthma, cancer, autism, and other diseases that affect children [7]. What is most problematic is that while low levels of exposure to many chemicals are unavoidable, scientists know little about the risks of such exposures. Added to this is the problem that scientists are frequently unable to distinguish which chemicals might be dangerous because people are exposed to so many simultaneously. Moreover, chemicals in the environment may act synergistically, meaning that their combined effect is greater than the sum of the effects of the individual chemicals.

Fast economic development and population growth result in continuing environmental degradation (Figure 1). For countries in the early stages of development the major environmental hazards to health are associated with widespread poverty and severe lack of public infrastructure, such as access to drinking water, sanitation, and lack of health care as well as emerging problems of industrial pollution. However, environmental health hazards are not limited to the developing world. Although at a lesser extend, environmental risks are also present in wealthier countries and are primarily attributed to urban air and water pollution. Occurrence of asthma is rising dramatically throughout the developed countries, and environmental factors appear to be at least partly responsible care [3]. The Millennium Ecosystem Assessment synthesis report [8] warns that the erosion of ecosystems could lead to an increase in existing diseases such as malaria and cholera, as well as a rising risk of new diseases emerging.

Climate change is also posing risks to human population health and well-being and thus is emerging as a serious concern worldwide "Climate change is the biggest global health threat of the 21st century" [9, 10, 11]. This is the jarring opening line of a report issued by the Commission on Climate Change that was jointly sponsored by *The Lancet* and University College of London's Institute for Global Health [12]. As stressed by the Intergovernmental Panel on Climate Change (IPCC), there has been a 0.17 °C rise in global average temperature since the beginning of the twentieth century and the rate of warming is expected to continue to increase as the current century unfolds. The 2014 IPCC report highlights the fact that in addition to a change in the global average temperature, other health, social, and environmental climate change impacts that have occurred to date have hit all regions of the world and have affected everything from access to food and water to exposure to extreme weather.

Figure 1. Intensification of agriculture, industrialization and increasing energy use are the most severe driving forces of environmental health problems.

The degradation of the environment, through air pollution, noise, chemicals, poor quality water and loss of natural areas, combined with lifestyle changes, may be contributing to substantial increases in rates of obesity, diabetes, diseases of the cardiovascular and nervous systems and cancer — all of which are major public health problems for Europe's population Reproductive and mental health problems are also on the rise. Asthma, allergies, and some types of cancer related to environmental pressures are of particular concern for children [13].

Environmental factors shape both infectious and non-infectious diseases, access to adequate diet, exposure to chronic stress, and even, going beyond the WHO definition, the impact of genetics on health. It can fairly be argued that the global health discourse on environmental health, despite its urgent tone at times, fails to fully acknowledge how fundamental the ways humans interact with their environments, built and "natural," are (and always have been) a key influence on the quality of human life. Today, with climate change among other disruptions of the environment produced by human actions, the stakes have risen considerably; indeed, in the eyes of some, the very sustainability of our species hangs in the balance.

Three frustrating challenges. As anthropologists, epidemiologists, and other social science researchers seek to address the growing problem of environmental health, they are hampered by three frustrating challenges (Table 2).

Table 2. Three Big Challenges for the Environmental Health

Challenge of attribution	It is difficult to definitively show that particular aspects or changes in the environment, including anthropogenic transformations, cause specific health consequences
Challenge of the elite contrarians	There are economically and politically powerful elite polluters and environmental disruptors who aggressively question undesirable research findings and actively resist regulation of contaminating and environmentally destructive behaviors
Challenge of partisan governance	Policy makers under the sway of elite polluters tend not to respond effectively or promptly to anthropogenic environmental health risks even when they are confirmed by extensive scientific research

Healthy city, healthy people. More than 75% of European people live in the cities therefore healthy cities also mean healthy people. The healthy cities project provides an excellent platform to enable concerted effort of all sectors of the community to work together in partnership to improve health in the place where we live, work and love.

Healthy Cities projects (Table 3) have six characteristics in common [14]:

Table 3. Healthy City provides:

- A clean, safe physical environment of high quality (including housing quality);
- An ecosystem that is stable now and sustainable in the long term;
- A strong, mutually supportive and non-exploitive community;
- A high degree of participation and control by the public over the decisions affecting their lives, health and wellbeing;
- The meeting of basic needs (for food, water, shelter, income, safety and work) for all the city's people;
- Access to a wide variety of experiences and resources, with the chance for a wide variety of contact, interactions and communication;
- A diverse, vital and innovative city economy;
- The encouragement of connectedness with the past, with the cultural and biological heritage of city dwellers and with other groups and individuals;
- A form that is compatible with and enhances the preceding characteristics;
- An optimum level of appropriate public health and sick care services accessible to all;
- High health status (high levels of positive health and low levels of disease).

Commitment to health. They affirm the holistic nature of health, recognizing the interaction between its physical, mental, social and spiritual dimensions. Promotion of health and prevention of disease are their priorities. They assume that health can be created through the cooperative efforts of individuals and groups in the city.

Political decision-making. They require political decision-making for public health. Housing, environment, education, social service and other programmes of city government have a major effect on the state of health in cities. Healthy Cities projects strengthen the contribution of such programmes to health by influencing the political decisions of city council.

Intersectoral action. They generate intersectoral action. The term "intersectoral action" describes the process through which organizations working outside the health sector change their activities so that they contribute more to health. Urban planning which supports physical fitness by providing ample green space for recreation in the city is an example of intersectoral action. Healthy Cities projects create organizational mechanisms through which city departments and other bodies come together to negotiate their contribution to such action.

Community participation. They emphasize community participation. People participate in health through their lifestyle choices, their use of health services, their views on health issues and their work in community groups. Healthy Cities projects promote more active roles for people in all of these areas. They provide means by which people have a direct influence on project decisions and, through the project, on the activities of city departments and other organizations.

Innovation. They work through processes of innovation. Promoting health and preventing disease through inter-sectoral action requires a constant search for new ideas and methods. The success of Healthy Cities projects depends upon their ability to create opportunities for innovation within a climate that supports change. Projects do this by spreading knowledge of innovative methods, creating incentives for innovation and recognizing the achievements of those who experiment with new policies and programs.

Healthy public policy. The success of Healthy Cities projects is reflected in the degree to which policies that create settings for health are in effect throughout the city administration. Projects achieve their goals when homes, schools, workplaces and other parts of the urban environment become healthier settings in which to live. Political decisions, inter-sectoral action, community participation and innovation promoted through Healthy Cities projects work together to achieve healthy public policy.

Globalization and the populations' health. There are various definitions relating to globalization. According to some, globalization has increased the significance of the integration of national economies in the global market through trade, investment and financial impact. Looking at it another way, this means a strong and complex global exchange of goods, services, finance, productivity and people. Labonte [15] defines globalization as a free, comprehensive and fast movement, exchange and transfer of information, knowledge, finances, goods, services and people between national economies globally. Globalization is not just a simple phenomenon, and not just an economic process, it contains new trends in the economy, leading to significant changes in the allocations of labor, as well as reorganization and relocation of companies

The process of globalization refers to a variety of interrelated processes. In fact, there are two primary components of globalization and can be associated to the deregulation of markets and investments. The next on importance follow the globalization of technologies (ICT), and cultural globalization. It is also important to note the emergence of globalization of ethical and judicial standards, which should ensure the social and individual rights.

From the standpoint of public health, globalization has a different meaning. On the one hand, rapid economic development and advanced technology have enabled health improvement and extension of the age of the population in the world. If we look at it in short terms, new developments and the modernization of society, and various medical and public-health programs have enabled the better health of the population. On the other hand, the impact of globalization jeopardizes the health of the population through the worsening social and economic conditions, the division of labor, increasing the "gap" between rich and poor, and the rapid expansion of consumption of consumer goods [16].

Global health. Global health and public health are indistinguishable. Both view health in terms of physical, mental, and social wellbeing, rather than merely the absence of disease. Both emphasize population-level policies, as well as individual approaches to health promotion. And both address the root causes of ill-health through a broad array of scientific, social, cultural, and economic strategies. Global health more emphasizes transnational health issues, determinants, and solutions; it involves many disciplines within and beyond the health sciences and promotes interdisciplinary collaboration; and it is a synthesis of population-based prevention with individual-level clinical care" [17]. Even so, the global health has not well-defined parameters. The area has evolved and changed its dimensions and challenges. No specific (formal) education/training, or defined curriculum have been offered for health professions.

CONCLUSION

Global and environmental health build on national policies, public health efforts and institutions. In many countries public health is equated primarily with population-wide interventions; global and environmental health are concerned with all strategies for health improvement, whether population-wide or individually based health care actions, and across all sectors, not just the health sector. *Health for all* refers back to the Alma Ata Declaration and positions global health at the forefront of the resurgence of interest in multi-sectoral approaches to health improvement and the need to strengthen primary health care as the basis of all health systems.

REFERENCES

1. Levy S, Wegman DH, Baron SL, and Sokas RK. Occupational and Environmental Health: Twenty-First Century Challenges and Opportunities. In Occupational and environmental health: recognizing and preventing disease and injury, Oxford University Press, 3-118 (2011).
2. United Nations Environment Programme and World Health Organization. Health & Environment Tools for Effective Decision-Making, UNEP/GRID Arendal, 1-27 (2004).

3. Pruss-Austun A., Corvalan C. Preventing disease through healthy environments: Towards an estimate of the environmental burden of disease, World Health Organization, 1-106 (2009).
4. Crain EF. Environmental threats to children's health: a challenge for pediatrics. Pediatrics 106 (4 Suppl): 871-875 (2000).
5. The National Training Institute for Child Care Health Consultants, , Environmental Health in Child Care Training Module version 4, UNC –CH, 1-67 (2013).
6. Monks V. Special report: Children at risk. National Wildlife Magazine 1997 (June/July).
7. Greater Boston Physicians for Social Responsibility. In harm's way: toxic threats to child development. Joint Project with Clean Water Fund, 1-149 (2000).
8. Millennium Ecosystem Assessment, 2005. Ecosystems and Human Well-being: Synthesis. Island Press, Washington, DC, 1-155 (2005).
9. Kovats RS, Haines A. Global climate change and health: recent findings and future steps. Can. Med. Assoc. J. 172:501–502 (2005).
10. Cifuentes L, Borja-Aburto VH, Gouveia N, Thurston G, Davis DL. Hidden health benefits of greenhouse gas mitigation. Science 17: 1257–1259 (2001).
11. Tol RSJ. Why worry about climate change? A research agenda. Environtal Values 17:437–470 (2008).
12. Lancet and University College London Institute for Global Health Commission. Managing the health effects of climate change. Lancet 373, 1693-1733 (2009).
13. EUR-LEX. Access to EU law. Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and The Committee of the Regions — Taking sustainable use of resources forward — A Thematic Strategy on the prevention and recycling of waste (2005).
14. WHO "Health topics: Environmental health". Retrieved 10 January 2015 (2015).
15. Labonte R., Torgerson R. Frameworks for analyzing the links between globalization and health. Draft report to the World Health Organization. Saskatoon, SPHERU, University of Saskatchewan, Scientific Res (2002).
16. Scholte JA. Globalization: a critical introduction, 2nd ed, Palgrave, New York, 1-400 (2017).
17. Koplan JP., Bond TC, Merson MH et al. Towards a common definition of global health. The Lancet, 373, 1993-1995 (2009).

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HONEYBEES (*Apis mellifera L.*) AS BIOINDICATORS OF METAL POLLUTION IN SERBIA

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ABSTRACT

Honeybees cover large areas and reflect the pollution present in water, air and soil. Our study included five different regions: Urban region (Belgrade), industrial region (Pančevo), thermal power plant region, agricultural region (Mesić), and a city with no heavy industry (Vršac). Aim of this study was to compare concentrations of Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Na, Ni, Sr, and Zn found in bodies of honeybees and to assess their origin. Statistically significant differences between locations were found for Ba, Cd, Co, Cr, Cu, Fe and Ni. PCA grouped the analyzed elements into three principal components based on their source.

Key words: bioindicator, honeybees, metal, pollution.

INTRODUCTION

The increase in human population has led to the increase in anthropogenic pollution. One of the main pollutants are toxic metals that burden soil, water, air, and other elements of the environment [1]. This pollution can come from various sources. Burning of fossil fuels in thermal power plants can lead to the increase in toxic metal concentrations in the environment [2]. The use of fertilizers, herbicides, pesticides, fungicides and insecticides in agriculture can leave metals as pollutants in the soil, air and water of agricultural areas [3]. In urban areas traffic is one of the main pollution sources [4].

Knowing that toxic metals can have negative effects on human health it is vital to monitor their concentrations in the environment. This leads to the development of methods that cost less, give faster results and cover bigger areas. Many different bioindicators have the mentioned properties and have been used for the monitoring of metals in the environment [5].

Since metals do not cause honeybee mortality, bees have been proposed as good bioindicators of metal pollution by many authors [6, 7]. They fly over an area of 7 km^2 sampling air, water, and soil through pollen and nectar they collect from plants [8].

The aim of this study was to measure concentration of Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Na, Ni, Sr, and Zn in bodies of adult honeybees collected twice during 2014 (July and September) at five different locations in Serbia.

MATERIALS AND METHODS

Research material were samples of honeybees obtained at three sampling sites in the region of thermal power plant "Kostolac" (TPP), two sampling sites in the cities of Belgrade (BG), an urban region, Pančevo (PA), industrial city, and Vršac (VS), which has no heavy industry, and one sampling site in the village Mesić (MS), an agricultural region.

Between 5 and 10 g of sample (50–100 bees) was collected from the outer frame of the hive that was occupied with bees but without brood. Samples were transferred into sterile plastic containers and frozen in the laboratory and kept at -21 ± 3 °C until analyzed.

Samples were measured and dried in the oven at 60 °C until constant mass. A test portion of dried sample between 0.5 and 1.0 grams was taken and digested according to the US EPA SW-846 Method 3052, under high pressure in closed Teflon vessels, with 7 ml of concentrated HNO_3 and 2 ml of concentrated H_2O_2. Mineralization was performed in a closed microwave digestion system (ETHOS 1, Advanced Microwave Digestion System, Milestone, Italy) by heating the samples up to 200 °C (15 min), followed by another 15 min at the same temperature. Each sample was cooled, transferred to a 25-mL volumetric flask and diluted to 25 mL with deionized water.

Quantitative determination of metals was performed by inductively coupled plasma–optical emission spectrometry, ICP-OES (iCAP 6500Duo, Thermo Scientific, Cambridge, UK). Multi-element standard solutions were used (Multi-Element Plasma Standard Solution 4, Specpure$^{®}$Alfa Aesar, Karlsruhe, Germany) for the determination of elements of interest. Quality control was based on the analysis of blanks (prepared following the whole sample preparation procedure), duplicates and analysis of the standard solutions.

The results were processed by one-way analysis of variance (ANOVA), followed by Tukey's HSD (Honestly Significant Difference) multiple comparisons test. Differences in concentrations were considered significant if p values were ≤ 0.05. Principal component analysis (PCA) was performed to assess the origin of analyzed metals.

RESULTS AND DISCUSSION

Mean concentrations of metals analyzed were calculated for each location, as well as standard deviations, and are given in Table 1. High standard deviations are present for some of the analyzed elements. This was to be expected because of the nature of the bioindicators used.

Using two-way ANOVA statistical differences between the analyzed locations were observed for Ba, Cd, Co, Cr, Cu, Fe and Ni. For the other elements no significant differences can be seen, suggesting similar exposer of honeybees in all five regions.

Ba had higher concentrations in MS compared to PA, VS and TPP, higher concentrations of Cd compared to VS, and highest concentrations of Ni compared to all other locations. Concentrations of Cr were higher in TPP in regard to VS. TPP region also had higher concentrations of Fe compared to PA and VS. Cu concentrations were statistically higher in BG compared to PA, TPP and VS.

Table 1. Mean metal concentrations in bodies of honeybees (mg kg^{-1} d.m.) and standard deviations

	Location				
Element	BG	PA	VS	TPP	MS
Al	24.04 ± 9.4	25.9 ± 8.3	16.8 ± 5.4	113 ± 110	29 ± 16
Ba	1.99 ± 0.7	1.05 ± 0.52	1.16 ± 0.72	1.74 ± 0.97	2.77 ± 0.7
Cd	0.15 ± 0.075	0.13 ± 0.12	0.086 ± 0.062	0.14 ± 0.091	0.21 ± 0.076
Co	0.14 ± 0.053	0.095 ± 0.085	0.062 ± 0.051	0.16 ± 0.06	0.11 ± 0.034
Cr	0.15 ± 0.047	0.163 ± 0.077	0.09 ± 0.04	0.36 ± 0.32	0.15 ± 0.068
Cu	25.7 ± 2.3	19.5 ± 6.8	16.4 ± 3.3	17.1 ± 3.1	21.8 ± 3
Fe	169 ± 37	133 ± 43	114 ± 49	247 ± 115	139 ± 43
Mn	52.4 ± 9.2	46 ± 17	30.1 ± 6.7	50 ± 17	61.1 ± 7.7
Na	406 ± 74	462 ± 126	432 ± 186	443 ± 142	454 ± 101
Ni	0.71 ± 0.18	0.51 ± 0.25	0.21 ± 0.11	0.86 ± 0.48	1.76 ± 0.33
Sr	2.14 ± 0.54	1.54 ± 0.90	1.88 ± 0.77	2.39 ± 0.7	2.17 ± 0.16
Zn	100 ± 16	104 ± 18	102 ± 46	101 ± 25	104 ± 12

To better explain this data PCA was performed (Table 2). PCA grouped the analyzed elements into three principal components (PC).

First PC is characterized by Ba, Ni and Cu, and to a lesser extent by Cd and Sr (Table 2). Ba and Ni had higher concentrations in MS, an agricultural area. The use of barium fluorosilicate and carbonate as insecticides contributes to the presence of Ba [9], Ni comes from artificial fertilizers [10], and Cu is the main component of Bordeaux mixture which is used as fungicide. Cu had higher concentrations in BG, an urban region, and this can be explained by high intensity traffic, as Cu is one of the main constituent of vehicle brake pads [11].

Al, Cr and Fe characterize the second PC (Table 2). ANOVA showed higher concentrations of Cr and Fe in the TPP region. These elements have been attributed to the use of coal in thermal power plants "Kostolac A and B" [12].

The third PC is mainly characterized by Zn, Na and Mn, and to a lesser extent by Cd (Table 2). These elements can have different origins. They can come from natural, as well as anthropogenic sources, mainly traffic. Zn and Cd are used in automotive industry [13]. The use of brakes, tires and other vehicle parts leads to release of these elements in the environment. Vehicle exhaust contains Na and Mn, among other elements [14].

Table 2. Principal component analysis (PCA) of heavy metals in bees (PCA loadings > 0.7 are shown in bold)

Element	Component		
	1	2	3
Ni	**0.817**	0.321	-0.038
Ba	**0.742**	0.470	0.167
Cu	**0.704**	0.038	0.331
Cd	0.640	-0.069	0.607
Sr	0.635	0.432	0.302
Co	0.554	0.497	0.464
Al	0.180	**0.882**	-0.136
Cr	0.150	**0.877**	0.250
Fe	0.279	**0.843**	0.249
Zn	0.077	0.028	**0.924**
Na	0.132	0.329	**0.754**
Mn	0.400	0.106	**0.739**
Initial Eigenvalues	6.123	1.975	1.121
Percentage of variance (%)	51.024	16.456	9.345
Cumulative percentage (%)	51.024	67.481	76.825

CONCLUSIONS

Some of the analyzed elements had statistically significant differences between the locations in this study. Mesić, an agricultural region had higher concentrations of Ba, Cd and Ni which come from fertilizers and insecticides used in agriculture. The mutual origin of these elements is confirmed by PCA. Higher concentrations of Cr and Fe in TPP region are from thermal power plants located in the region. High Cu content in honeybees from BG, an urban region are explained by intense traffic.

This study shows that honeybees can be a good bioindicator that can detect trace elements present in the environment. They are capable of distinguishing different concentrations of metals in different foraging regions and can be used to assess the sources of these metals.

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REFERENCES

1. Diels L, Van Der Lelie N, Bastiaens L (2002) New developments in treatment of heavy metal contaminated soils. Environ Sci Biotechnol 1(1):75–82
2. Pudasainee D, Kim J-H, Lee S-H, Park J-M, Jang H-N, Song G-J, Seo Y-C (2010) Hazardous air pollutants emission from coal and oil fired power plants. Asia-Pac J Chem Eng 5(2):299–303

3. Mortvedt JJ (1996) Heavy metal contaminants in inorganic and organic fertilizers. Fert Res 43(1–3):55–61
4. Silva LT, Pinho JL, Nurusman H (2014) Traffic air pollution monitoring based on an air–water pollutants deposition device. Int J Environ Sci Technol 11(8):2307–2318
5. Garcı´a-Herna´ndez J, Hurtado LA, Leyva-Garcı´a G, Gu¨ido-Moreno A, Aguilera-Ma´rquez D, Mazzei V, Ferrante M (2015) Isopods of the genus Ligia as potential biomonitors of trace metals from the Gulf of California and pacific coast of the Baja California peninsula. Ecotox Environ Safe 112:177–185
6. Leita L, Muhlbachova G, Cesco S, Barbattini R, Mondini C (1996) Investigation on the use of honeybees and honeybee products to assess heavy metals contamination. Environ Monit Assess 43(1):1–9
7. Porrini C, Ghini S, Girotti S, Sabatini AG, Gattavecchia E, Celli G (2002) Use of honeybees as bioindicators of environmental pollution in Italy. In: Deville's J, Pham-Delegate MH (eds) Honey bees: estimating the environmental impact of chemicals. Taylor & Francis, London, New York, pp 186–247
8. Perugini M, Manera M, Grotta L, Abete MC, Tarasco R (2011) Heavy metal (Hg, Cr, Cd, and Pb) contamination in urban areas and wildlife reserves: honeybees as bioindicators. Biol Trace Elem Res 140(2):170–176
9. Meister RT (2004) Crop protection handbook. Meister Media Worldwide, Willoughby
10. Gonnelli C, Renella G (2013) Chromium and nickel. In: Alloway BJ (ed) Heavy metals in soils, 22. Springer, Netherlands, pp 313–333
11. Christoforidis A, Stamatis N (2009) Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. Geoderma 151(3–4):257–263
12. Zarić, N. M., Ilijević, K., Stanisavljević, L., & Gržetić, I. (2016). Metal concentrations around thermal power plants, rural and urban areas using honeybees (Apis mellifera L.) as bioindicators. *Int J Environ Sci Technol*, 13(2), 413-422.
13. Whiley AJ (2011) Copper and zinc loading associated with automotive brake-pad and tire wear, water quality program. Washington State Department of Ecology Olympia, Washington
14. Spengler, J., Lwebuga-Mukasa, J., Vallarino, J., Melly, S., Chillrud, S., Baker, J., & Minegishi, T. (2011). Air toxics exposure from vehicle emissions at a U.S. border crossing: Buffalo Peace Bridge Study. Research report (Health Effects Institute), 158, 5-132.

METAL CONTENTS OF WHITE, ROSE AND RED WINES FROM SERBIA

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ABSTRACT

There is a growing number of wine makers in Serbia. This is the reason that wine needs to be monitored regularly. The aim of this study is to determine concentrations of Pb, Cd, As, Sn, Zn, Fe, Cu, Mn and Ni in white, rose and red wines from Serbia, and to assess risks to health. None of the examined wines had concentrations of the analyzed elements above the maximum permitted concentration. Furthermore, none of the wines had THQ values higher than 1. From this it can be concluded that there is no risk in consuming 250 ml of these wines per day.

Key words: Metals, Wine, THQ, Risk Assesment.

INTRODUCTION

Wine is made up of ethanol, water, saccharides, phenolic compounds, and other pigments [1, 2]. Minerals are another important component of wine [3]. There are different factors that affect trace element composition of wine. These factors include mineral composition of the soil, viticulture practices, environmental factors, fermentation process, clarification procedure, and storage conditions [4]. Moreover, specific production area, climate and grape variety also influences trace element content in wine [4]. Content of metals generally decrease during fermentation processes. The increase in metal concentrations happens because of post fermentation processes contamination [5].

Knowing metal content of wine is important because they influence wine quality and can have an effect on human health [6]. To estimate potential health risks associated with long term exposure to chemical pollutants the US environmental protection agency (USEPA) has developed target hazard quotients (THQ) [7]. Each country also has regulations stating the maximal content of different metals in wine. In Serbia maximum concentrations of Pb, Cd, As, Sn, Zn, Fe and Cu are 0.2, 0.1, 0.2, 10, 5, 10, and 3 mg/l respectively [8]. There is no regulation for the content of Mn and Ni.

The aim of this study is to determine metal concentrations of Pb, Cd, As, Sn, Zn, Fe, Cu, Mn and Ni in different wines from Serbia, see whether they are in accordance with local regulations and to assess if there are any differences in metal content in different types of wine. Moreover, THQ levels are to be calculated for each wine type (white, rose, red) for man and for women.

MATERIALS AND METHODS

Three different types of wine were tested: white, red and rose; six different white wines, two rose wines, and five red wines, all from different manufacturers were selected and labeled 1 – 13.

Before analysis samples were diluted with 1 % HNO_3 in a ratio of 1:10. Six point matrix matching calibration was performed, with alcohol and HNO_3. The calibration ranged from 0.05 ml/l to 1 mg/l. Quantitative determination of metals was performed by inductively coupled plasma–optical emission spectrometry, ICP-OES, Agilent 5100. Recoveries was checked by using spiked samples. Recoveries for Pb ranged from 84 – 105 %, Cd 83 – 103 %, As 88 – 121 %, Cu 94 – 118 %, Fe 91 – 109 %, Zn 90 – 107 %, Sn 93 – 138 %.

Limits of quantification (LOQ) were determined: Pb 0.02 mg/l, Cd 0.02 mg/l, As 0.05 mg/l, Sn 0.1 mg/l, Zn 0.05 mg/l, Fe 0.05 mg/l, Cu 0.05 mg/l, Mn 0.02 mg/l, and Ni 0.02 mg/l.

Data were statistically processed using SPSS. ANOVA with Tukey's post – hoc test was used to assess differences in metal concentrations between different types of wine. THQ was calculated by the formula provided by USEPA [7].

$$THQ = \frac{Efr \times EDtot \times SFI \times MSC}{RfD \times BW \times AT} \times 10^{-3}$$

Where Efr is the exposure frequency (days/year) which was in this case 365 days; EDtot is the exposure duration set by average life expectancy of 77.9 years for women and 72.8 years for man with consumption starting at the age of 18, which gives as EDtot (male) = 20 002 days, EDtot (female) = 21 863.5 days; SFI is the mass of wine ingested, in this case 250 ml/day; MSC is the concentration of the element in question (mg/kg); RfD is the oral reference dose (mg/kg/day): Pb = 0.004, Cd = 0.001, As = 0.0003, Zn = 0.3, Fe = 0.7, C = 0.04, Mn = 0.14, Ni = 0.02; BW is the body weight, for man in Serbia it is 86 kg, and for women 63 kg; AT is average time for non-carcinogens whish was determined to be 30 years by USEPA.

RESULTS AND DISCUSSION

Concentrations of analyzed metals in wine are given in table 1. As can be observed for Cd and As all analyzed samples had concentrations under the limit of quantification (LOQ). Concentrations of Ni were above LOQ in only one sample of white wine. Pb had values under LOQ for half of the white wine samples, and almost all of red wine samples. Concentrations of Pb in rose wine samples was in all cases above

LOQ. Concentrations of Sn and Zn were below LOQ in the same white wine sample. Fe concentrations were under limit of quantification in one rose wine, while Mn had concentrations below LOQ in one white wine sample. Two white wine samples had concentrations of Cu under the quantification limits.

Serbian regulations have set values for maximum permitted concentrations (MPC) of Pb, Cd, As, Sn, Zn, Fe and Cu in wine. For Mn and Ni no regulations are in effect concerning their concentrations in food or drinks. None of the analyzed samples of wine exceeded MPC limits (Table 1).

Analysis of variance (ANOVA) followed by Tukey's post – hoc test was used to determine whether there are statistically significant differences among metal concentrations in the analyzed wine. Only significant differences were observed for Pb. The analyses showed that rose wines had significantly higher concentrations of Pb compared to white or red wines. For the rest of the analyzed metals there were no statistically significant differences.

Table 1. Metal concentrations in wine, and maximal permitted concentrations (MPC)

Wine	Type	Pb	Cd	As	Sn	Zn	Fe	Cu	Mn	Ni
1	White	< 0.02	< 0.02	< 0.05	0.59	0.34	0.84	0.06	2.00	0.05
2	White	< 0.02	< 0.02	< 0.05	0.67	0.26	0.46	< 0.05	0.66	< 0.02
3	White	< 0.02	< 0.02	< 0.05	0.62	0.25	1.03	0.49	0.98	< 0.02
4	White	0.03	< 0.02	< 0.05	< 0.10	< 0.05	0.29	< 0.05	< 0.02	< 0.02
5	White	0.03	< 0.02	< 0.05	0.58	0.14	3.07	0.06	0.66	< 0.02
6	White	0.02	< 0.02	< 0.05	0.56	0.31	3.59	0.66	0.73	< 0.02
7	Rose	0.09	< 0.02	< 0.05	0.61	0.29	< 0.05	0.15	0.73	< 0.02
8	Rose	0.1	< 0.02	< 0.05	1.03	0.56	4.58	0.05	1.26	< 0.02
9	Red	0.04	< 0.02	< 0.05	0.52	0.44	2.16	0.87	1.11	< 0.02
10	Red	< 0.02	< 0.02	< 0.05	0.47	0.42	1.67	0.13	1.24	< 0.02
11	Red	< 0.02	< 0.02	< 0.05	0.62	0.28	0.48	0.1	0.98	< 0.02
12	Red	< 0.02	< 0.02	< 0.05	0.51	0.42	2.1	0.82	1.06	< 0.02
13	Red	< 0.02	< 0.02	< 0.05	0.61	0.3	2.11	0.49	1.22	< 0.02
MPC		0.2	0.1	0.2	10.0	5.0	10.0	3.0	-	-

THQ values that are greater than 1 are to cause concern. Considering that in this study all THQ values were below 1, there is no need for concern that metal concentrations in these wines can cause negative health effects (Table 2).

Table 2. Target hazard quotients (THQ) for males and females, and different wine types

	THQ (male)			THQ (female)		
Element	White	Rose	Red	White	Rose	Red
Pb	0.0113	0.0460	0.0116	0.0169	0.0687	0.0174
Cd	0.0384	0.0388	0.0388	0.0574	0.0578	0.0578
As	0.1615	0.1615	0.1615	0.2410	0.2410	0.2410
Zn	0.0015	0.0027	0.0024	0.0022	0.0041	0.0036
Fe	0.0043	0.0064	0.0047	0.0064	0.0096	0.0070
Cu	0.0111	0.0048	0.0234	0.0165	0.0072	0.0348
Mn	0.0117	0.0138	0.0155	0.0174	0.0206	0.0232
Ni	0.0024	0.0019	0.0019	0.0036	0.0029	0.0029

CONCLUSIONS

Of the analyzed elements Cd and As were below the LOQ in all wine samples. Ni was above LOQ in only one sample. For some of the other elements concentrations were in some wines also under the LOQ.

All of the analyzed elements had concentration that were below maximum permited concentrations.

None of the elements had target hazard quotients above; so none of them pose any risk to human health if consumed in moderation (250 ml/day).

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REFERENCES

15. Nilsson M., Duarte I.F., Almeida C., Delgadillo I., Goodfellow B.J., Gil A.M., Morris G.A. (2004): High-resolution NMR and diffusion-ordered spectroscopy of port wine. Journal of Agricultural and Food Chemistry, 52: 3736–3743.
16. Roig B., Thomas O. (2003): UV monitoring of sugars during wine making. Carbohydrate Research, 338: 79–83.
17. Monaci F., Bargagli R., Focardi S. (2003): Element concentrations in Chianti Classico appellation wines. Journal of Trace Elements in Medicine and Biology, 17: 45–50.
18. Núñez M., Peña R.M., Herrero C., García-Martín S. (2000): Analysis of some metals in wine by means of capillary electrophoresis. Application to the differentiation of Ribeira Sacra Spanish red wine. Analysis, 28: 432–437.

19. Ibanez J.G., Carreon-Alvarez A., Barcena-Soto M., Casillas N. (2008): Metals in alcoholic beverages: A review of sources, effects, concentrations, removal, speciation and analysis. Journal of Food Composition and Analysis, 21: 672–683.
20. Lara, R., Cerutti, S., Salonia, J. A., Olsina, R. A., & Martinez, L. D. (2005). Trace element determination of Argentine wines using ETAAS and USN-ICP-OES. Food and Chemical Toxicology, 43, 293–297.
21. U.S. EPA, Guidance manual for assessing human health risks from chemically contaminated, fish and shellfish, U.S. Environmental Protection Agency, Washington, D.C. (1989) EPA-503/8-89-002.
22. PRAVILNIK o dopuni Pravilnika o maksimalno dozvoljenim količinama ostataka sredstava za zaštitu bilja u hrani i hrani za životinje i o hrani i hrani za životinje za koju se utvrñuju maksimalno dozvoljene količine ostataka sredstava za zaštitu bilja. Broj 110-00-00001/2011-09. 26. april 2011.

CONTRIBUTION OF URBAN GARDENS TO FOOD SECURITY IN CITIES. A CASE STUDY OF THE CITY OF KRAGUJEVAC

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ABSTRACT

Growing concerns about the quality and affordability of food, in circumstances of rapid urbanization and increase in urban poverty worldwide, has renewed interest in the integration of urban agriculture in sustainable urban development. Urban gardens, including community gardens, allotments and home gardens, are places where food is grown locally in cities. Those are important multifunctional components of urban green infrastructure and productive landscape. The aim of this article is to examine the role of urban home gardens in the household food security. We collected data from semi-structured interviews with fourteen gardeners in five suburban neighbourhoods in Kragujevac. The results suggest a significant role of urban gardens in health and well-being of gardeners, principally in the production of healthy and fresh fruits and vegetables.

Key words: urban gardens, urban agriculture, food security, semi-structured interviews.

INTRODUCTION

Urban development of contemporary cities faces major challenges that are related to rapid urbanization. With the prospect of world population of 9.6 billion by 2050 (United Nations, 2013) and increase in urban population from 50% nowadays to 70% by 2030, food security becomes one of the major issues in cities worldwide. Number of people involved in urban agriculture has never been higher. Food and Agriculture Organization estimates that there are 100 million people involved in urban agriculture (FAO, 1996).

Urban gardening is a component of urban agriculture that has become very popular in the past decades (Ruggeri et al., 2016). Urban gardens are component of green infrastructure that perform multiple functions, from environmental (Cameron et al, 2012; Eigenbrod and Gruda, 2015), recreational (Cameron et al, 2012, Dewaelheyns et al., 2015), educational (Eigenbrod and Gruda, 2015) to food production (Kortright and Wakefield, 2011; CoDyre at al., 2015; Camps-Calvet et al., 2016). Ruggeri et al. (2016) use the term „urban gardening" to refer to no-profit process of intensive growing of every type or variety of plants en plein air urban environment. Turner and Henryks

(2012) identify three main categories of urban gardens: home gardens, allotment gardens and community gardens.

Home gardens are the most common form of urban agriculture (Taylor and Lovell, 2014). Loram et al. (2007) estimate that home gardens occupy 35-47% of urban green areas in UK (as cited in Cameron et al., 2012). Home gardens cover 16% of the central territory of the city of Stockholm in Sweden (Dewaelheyns, 2014). Kortright and Wakefield (2011) define a home food garden as "a fruit and/or vegetable garden on leased, owned, or borrowed land directly adjacent to the gardener's residence". For the purpose of this study we further limit the definition to gardens managed by a single family.

Urban home gardens have existed as long as there have been cities and have contributed to household livelihoods and food security of urban dwellers through cultivation of trees, shrubs and herbaceous plants (Taylor and Lovell, 2010). Food security is defined by Food and Agriculture Organization (1996) to mean the condition "when all people, at all times, have physical and economic access to safe and nutritious food which meets their dietary needs and food preferences for an active and healthy life". Home gardens affect food security in many ways, including accessibility, nutrition, safety, self-reliance, and environmental sustainability, at different levels such as individual, household, and level of the neighborhood (Kortright and Wakefield, 2011).

Many studies argue that food security is especially a problem in developing countries (CoDyre at al., 2015; Eigenbrod and Gruda, 2015). Motivations for urban gardening differ considerably in developed countries, having social and educational benefits as main reasons for gardening activities (Eigenbrod and Gruda, 2015). Even though urban gardens are not the most important source of food for city-dwellers, they can provide an important supplement or alternative to diets, and serve as backup supply during times of scarcity or disruption (Kortright and Wakefield, 2011). This proved to be the case in some of the countries in South Eastern Europe during the periods of economic hardship (Chisholm, 1996; Yoveva et al., 2000). Home gardens helped overcome food shortages in Sofia, capital of Bulgaria, during the crisis in 1990s, by supplementing diets of low-income urban families (Yoveva et al., 2000).

Still, only few studies have addressed the question of urban gardens in the countries of the South Eastern Europe. Furthermore, previous work on urban gardening has largely focused on collective gardens, paying little attention to home gardens, an ever present and more durable form of urban agriculture (Taylor and Lovell, 2014). The characteristics of home gardens, reasons for gardening and role of urban home gardens in households' well-being and nutrition have not been coped with in depth.

The aim of this paper is to deepen the understanding of the contribution of home gardens to households' well-being and food security. In the case study of the city of Kragujevac we examine the motivations for gardening and the role of food production as one of the key functions of home gardens.

MATERIALS AND METHOD

The research is conducted in the form of a case study. Exploratory nature of the study and qualitative approach allow us to reach a better understanding of the matter.

The reasons for selection of the city of Kragujevac for the study site are manifold. Kragujevac is one of the cities which have adopted the Sustainable Development Strategy. The city administration has generally approved the strategy of "neo-endogenous development" which indicates focusing on inner resources and revaluation of the local culture and traditions, regional food and natural resources (Petrović and Toković, 2016). The Strategy identifies the potential for city's integration with the wider surrounding in the domain of agriculture (Petrović and Toković, 2016).

A total of fourteen in-depth semi-structured interviews were conducted from late February to the end of March 2017 with gardeners in five suburban neighbourhoods (Vinogradi, Grošnica, Ilina voda, Bresnica, Male Pčelice) (Fig. 1).

We performed snowball sampling method. Interviews lasted between 40 minutes and an hour. The interview process would start with exploring and photographing of participants' gardens (Taylor and Bogdan, 1998) to document the proportion of the space devoted to food garden and ornamental garden. After completing the interviews, we conducted the transcription of audio recordings, and field observations were written down in the form of notes.

The questions are clustered in following thematic areas: gardeners' motivations, the role of gardens in households' nutrition, productivity of home gardens and general socioeconomic characteristics of households. The data obtained from closed-ended questions were coded and processed by the statistical descriptive method.

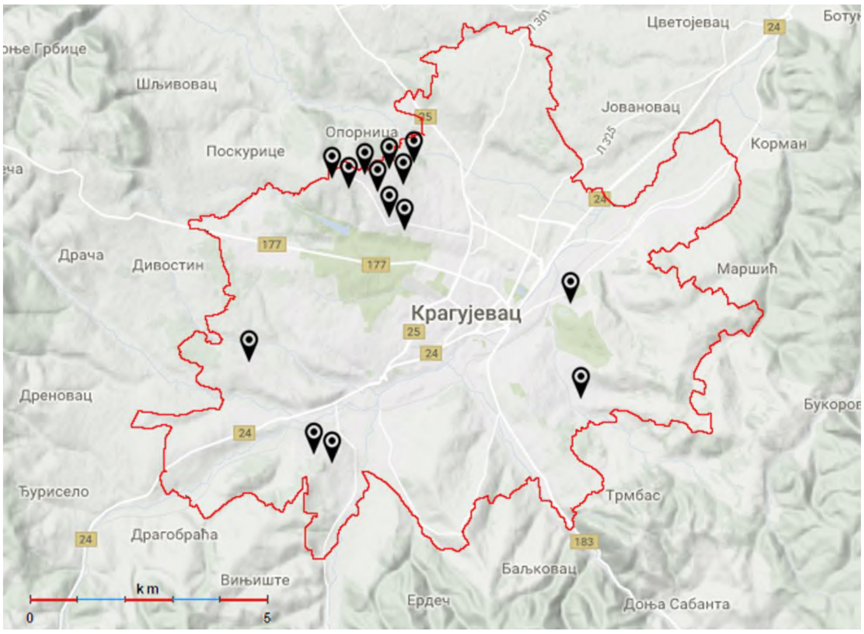

Figure 1. Locations of gardens
(**source:** Čepić and Tomićević-Dubljević, in press)

RESULTS AND DISCUSSION

The age of the interviewees ranges from 24 to 73 years old, while the average is 56 years. Of the fourteen respondents, the majority is male (57%) and 43% are female. More than half of the interviewees have a university degree (57%), 36% have a secondary education diploma and 7% have completed the elementary school level. Families with more than four members make 36% of the sample, 36% are four-member families and 28% count less than four members. Almost half of the participants are in retirement (43%), 21% are unemployed and 36% are employed.

Firstly, we wanted to explore motivations for gardening among participants and gain understanding of the role of food production as one of the functions of home gardens. In response to the open-ended question "What are your reasons for gardening?" 71% of interviewees responded that it is a healthy food. Most of the participants expressed concern for the healthy nutrition, especially of their children and grandchildren. For them, the most important benefit of gardening is production of fresh and healthy fruits and vegetables under controlled conditions, with minimal use of chemical pesticides. Other mentioned reasons are leisure and recreation, economic benefits, market place being far away, spending time outdoors, garden as a challenge and a hobby, education of children (Table 1).

Table 1. Reasons for gardening

Reasons for gardening	Healthy and fresh food	Leisure and recreation	Economic benefits	Education of younger generations	Market place is far away	Garden as a challenge and experiment
Frequency (n=14)	71%	36%	29%	14%	14%	7%

Furthermore, we examined the role of gardens in households' nutrition. When asked „Who consumes fruits and vegetables from the garden?", all of the interviewed families confirmed that members of the household are the primary users. The majority of respondents (87%) share the produce with extended family. Interestingly, more than half of the interviewed households (57%) share surpluses with neighbours and friends. All of the participants said that they process part of the fruit and vegetables from the garden and conserve it for the winter. They do it every year. For most of the participants having supplies of stored food in the home increases the family's food security and it has proved to be especially important in the times of crisis. Fruits, vegetables and herbs from the garden are consumed almost every day, fresh during the harvest season and conserved in winter, as reported by all of the interviewees. Similar consumption habits are reported by Yoveva et al. (2000) in the investigated households in the city of Sofia, where a large part of the produce is used for subsistence of the gardeners. Part of the fruits and vegetables are processed and conserved for winter.

In response to the question "To what extent do fruits and vegetables from the garden meet the dietary needs of your family?", most of those interviewed (86%) replied that they are self-sufficient in most of the produce through the harvest season so they do not need to purchase those varieties of fruits and vegetable that they produce. The remaining 14% of respondents reported that they produce 50-80% of the amount of fruits and vegetables that their households consume and that they buy the rest.

When asked "Do you think that you would eat smaller amounts of fruits and vegetables if you would not have a garden?", 57% of the interviewed households agreed, 14% were not sure and 28% believe that they would consume equal amounts of fruits and vegetables. Similarly, 78% of participants believe that their diet is more diverse due to the fact of having a garden, while 22% assume that having a garden does not affect the diversity of their nutrition. These results support previous findings by Kortright and Wakefield (2011) that gardens increase gardeners' consumption of fresh produce. Taylor and Lovell (2014) outline several studies that have found a positive correlation between the diversity and quantity of fruits and vegetables consumed and access to or ownership of a garden. Having a garden with fruits and vegetables close to the place of residence makes it easier to eat fresh food more often.

Investigated gardens vary in size from 100 m² to 700 m², with 260 m² being the average. The amount of vegetables produced in gardens during one year is in the range of 0.54 kg / m² to 6.25 kg / m², with 2.86 kg / m² being the average. Compared to other studies conducted in cities with similar climate, this is a relatively higher production. CoDyre et al. (2015) reported the average1.43 g / m² of fruit and / or vegetables produced in one year in private urban gardens in the city of Guelph, medium-sized town not far from Toronto.

The gardens investigated in this study included a wide variety of crops. There are more than twenty different types of vegetables, out of which tomato, cucumber, onion, garlic, carrots, potatoes, peppers, peas, green beans and cabbage are grown in more than 50% of households participating in the research (Table 2). More than twenty species of fruit trees and shrubs are identified, with plum and apple being the most common species. Interestingly, 62% of interviewed gardeners grow chokeberries (Aronia sp.), which are non-native shrubs in this region and have become popular among gardeners only in the past decade. This confirms the indication of some authors that home gardens are important contributors to urban biodiversity (Cameron et al., 2012; Dewaelheyns, 2014). Gardeners have always been interested in exotic and unusual plant species (Cameron et al., 2012), which is why gardens accommodate a larger proportion of alien species compared to other type of green areas. In addition to vegetables and fruits, we have identified different types of herbs grown in majority of gardens such as parsley, mint, rosemary, sage.

Table 2. Most common types of vegetables and their average yields

Vegetables	Prevalence in gardens (%)	Yield per garden in one year (kg)
tomato	100%	180
cucumber	85%	64
beet	46%	14
onion	92%	45
garlic	85%	5
carrot	69%	13
potato	92%	103
paprika	54%	164
peas	69%	14
green beans	69%	24
cabbage	77%	51

Of the interviewed households, 43% have a greenhouse in the garden where they grow early spring vegetables. The size of the greenhouses varies from 24 m² to 60 m², with an average of 43 m². Participants explained that the most important reason for initiating the greenhouse production of vegetables are fresh produce at the beginning of the harvest season, when they are the most expensive.

CONCLUSIONS

Home gardens are widespread vernacular elements of urban and peri-urban landscapes of Serbian cities. They provide diverse benefits to gardeners, from social, economic to environmental. The case study of the city of Kragujevac helps us better understand reasons why people engage in gardening and the role of food production among other functions of the garden. It allows us to estimate the actual food production capacity of home gardens and expand knowledge of diversity of fruits, vegetables and other plant species grown in home gardens. Although the results of the research cannot be used to generate general conclusions because of the small sample size, they do create a solid understanding of the matter. The most important motivation for gardening that was identified in the study is healthy and fresh food. The role of food production seems to be dominant, among other functions that gardens perform, such as recreation and hobby, household economic benefits, etc. The study indicates that having fruits and vegetables easily accessible to household members stimulates larger intake of fruits and vegetables among family members and allows for higher diversity of fresh and nutritious produce. This is the most significant way in which home gardens affect household food security.

This research is the first exploratory study of urban home gardens in Serbia. The aim of the research is to provide an initial step towards the understanding of the role that urban gardens have in the sustainable development of Serbian cities. Future research is needed to quantify the benefits of urban gardens using representative samples from different cities of Serbia. This would help establish a more comprehensive database of garden functions and better evaluate food productivity of home gardens.

REFERENCES

1. Cameron, R. W. F., Blanusa, T., Taylor, J. E., Salisbury, A., Halstead, A. J., Henricot, B., Thompson, K. (2012). The domestic garden – Its contribution to urban green infrastructure. *Urban Forestry & Urban Greening, 11*, 129-137
2. Camps-Calvet, M., Langemeyer, J., Calvet-Mir, L., Gómez-Baggethun, E. (2016). Ecosystem services provided by urban gardens in Barcelona, Spain: Insights for policy and planning. *Environmental Science & Policy (2016),* http://dx.doi.org/10.1016/j.envsci.2016.01.007
3. Chisholm, A. (1996). *City Farming In Albania.* Retrieved from http://www.cityfarmer.org/albania.html
4. CoDyre, M., Fraser, E.D.G, Landman, K. (2015). How does your garden grow? An empirical evaluation of the costs and potential of urban gardening. *Urban Forestry & Urban Greening, 14*, 72-79

5. Čepić, S., Tomićević-Dubljević, J. (in press). Značaj urbanih bašta u kontekstu održivosti životne sredine u gradovima. Studija slučaja grada Kragujevca. *Ecologica*.
6. Eigenbrod, C., Gruda, N. (2015). Urban vegetable for food security in cities. A review. *Agronomy for Sustainable Development, 35*, 483–498.
7. Dewaelheyns, V. (2014). *The Garden Complex In Strategic Perspective: The Case of Flanders* (Doctoral dissertation). Retrieved from https://lirias.kuleuven.be/bitstream/123456789/465722/1/PhD_ValerieDewaelheynsLowQuality.pdf
8. Dewaelheyns, V., Lerouge, F., Rogge, E., Vranken, L. (2015, May). *A Different Perspective on Garden Grabbing: Mapping the Adaptive Capacity of Home Food Production.* Paper presented at REAL CORP 2015: Plan Together – Right Now – Overall. From Vision to Reality for Vibrant Cities and Regions, Ghent, Belgium.
9. FAO (1996). The state of food and agriculture. Retrieved from http://www.fao.org/docrep/003/w1358e/w1358e00.htm
10. Kortright, R., Wakefield, S. (2011). Edible backyards: a qualitative study of household food growing and its contributions to food security. *Agriculture and Human Values, 28*, 39-53.
11. Petrović, M., Toković, M. (2016). Neoendogeni razvoj gradova i ekološki paradoks: studija slučaja šest gradova u Srbiji. *Sociologija, 58 (suppl. 1)*, 181-209.
12. Ruggeri, G., Mazzocchi, C., & Corsi, S. (2016). Urban gardeners' motivations in a metropolitan city: the case of Milan. *Sustainability 2016, 8*, 1099
13. Taylor - Lovell, S. (2010). Multifunctional Urban Agriculture for Sustainable Land Use Planning in the United States. *Sustainability 2010, 2*, 2499-2522
14. Taylor, J. R., Lovell, S. T. (2014). Urban home food gardens in the Global North: research traditions and future directions. *Agriculture and Human Values, 31*, 285–305.
15. Taylor, S. J., & Bogdan, R. (1998). Introduction to qualitative research methods: A guidebook and resource. New York: Wiley
16. Turner, B., Henryks, J. (2012, August). A Study of the Demand for Community Gardens and their Benefits for the ACT Community: Report Prepared for The Environment and Sustainable Development Directorate ACT. Retrieved from http://www.planning.act.gov.au/__data/assets/pdf_file/0017/34145/20130402_Community_Gardens_ACT_-_University_of_Canberra_-_Final_Report.pdf
17. United Nations (2013). *World population prospects. Highlights and advance tables*. Retrieved from https://esa.un.org/unpd/wpp/Publications/Files/WPP2012_HIGHLIGHTS.pdf
18. Yoveva, A., Gocheva, B., Voykova, G., Borissov, B., & Spassov, A. (2000). Sofia: Urban Agriculture in an Economy in Transition. In N. Bakker, M. Dubbeling, S. Guendel, U. Sabel Koschella, H. de Zeeuw (eds.), *Growing Cities, Growing Food, Urban Agriculture on the Policy Agenda* (501-518). DSE.

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DEGRADATION OF HERBICIDES WITH CHLORINE DIOXIDE: DEGRADATION EFFICIENCY AND TOXICITY TEST

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ABSTRACT

The main objective of this study was to find optimal parameters for degradation of herbicides, such as nicosulfuron and thifensulfuron-methyl, with chlorine dioxide in deionized water. In order to examine the optimal parameters, degradation of herbicides was investigated under light or dark conditions with different amount of chlorine dioxide (5 and 10 ppm), different time of degradation (30 min, 1, 2, 3, 6 and 24 h) and at different pH values (3, 7 and 9). Degradation efficiency of herbicides was monitored using HPLC-DAD. Acute toxicity tests were performed for degradation products after the treatment with chlorine dioxide.

Key words: herbicides, chlorine dioxide, HPLC, degradation efficiency, toxicological analysis.

INTRODUCTION

Pesticides are very hazardous pollutants that can persist in the aquatic environment for many years [1]. Contamination of soil and ground water by pesticides applied to soil and swept by transport processes such as leaching or runoff is posing an increasingly serious environmental problem. Besides that, herbicides are one of the most used groups of organic compounds, especially for treatments in agro- and horticulture [2]. They are used for weed control in crops. The weed reduces the yield, increases the cost of agricultural production and can reduce crop quality [3]. The widespread use of herbicides and pesticides are in general in agricultural and non-agricultural purposes, and has resulted in the presence of their residues in the various environmental matrices [4]. The land becomes contaminated from the use of herbicides, which are well soluble in water. They, as well as their degradation products, are washed away and get into ground waters, thereby contaminating them [5, 6].

Nicosulfuron, chemically defined as 2-[(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoyl]-N,N-dimethylpyridine-3-carboxamide (NS; Figure 1), and thifensulfuron-methyl, chemically defined as methyl 3-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoylsulfamoyl]thiophene-2-carboxylate (TFSM; Figure 1) are sulfonylurea herbicides typically used to control weeds in post-emergence treatments. Several authors have studied different properties of nicosulfuron pesticide such as its degradation or its effect in the grown of different vegetables. Adsorption and desorption of nicosulfuron in soils [7, 8] and clay minerals [9] have been studied.

Accordingly, in order to reduce the harmfulness of pesticide residues, different treatments are used for their degradation and removal. One way is by using chlorine dioxide (ClO_2) [10]. Chlorine dioxide is a very powerful means for the disinfection and highly selective oxidizing agent ($E_0 = 0.936$ V), so that it can selectively oxidize specific functional groups such as phenolic groups, and tertiary amines [11, 12]. It achieves a very high solubility in water, especially cold. Chlorine dioxide decomposes under the influence of UV rays, high temperature and pH>12. It should not be stored for a long time because it slowly dimerizes to chlorine and oxygen. It is suitable for the treatment of apples, lettuce and the minced meat in order to reduce the microbial activity, for the degradation of certain drugs, as well as for the removal of pesticides on fresh fruits and vegetables [13, 14]. In literature there were data for removal of isoproturon, ametryn, methiocarb, phorate, diazinon and phenylurea pesticides [15, 16, 17, 18]. Chlorine dioxide is used as a disinfecting/oxidizing agent in the treatment of drinking water. In comparison with chlorine, it has a stronger antimicrobial activity, and compared with the ozone and chlorine does not give toxic products such as trihalo-methane, halogen acids and ketones. The disadvantage of chlorine dioxide is in the fact that chlorine dioxide is transformed into chlorite and chlorate anion during treatment (about 70% of chlorine dioxide is transformed in chlorite and 10% in chlorate), which have a negative impact on human health, because they lead to changes in the red blood cells.

Chlorine dioxide was efficiently used for degradation of sulfonylurea herbicides: thifensulfuron-methyl and nicosulfuron. This is the first study of degradation of these herbicides with chlorine dioxide. The objectives of this study were to: a) investigate and optimize degradation of sulfonylurea herbicides: thifensulfuron-methyl and nicosulfuron, with chlorine dioxide in deionized water, b) investigate degradation efficiency of herbicides using HPLC-DAD, and c) examine toxicity of degradation product of herbicides after chlorine dioxide treatment.

MATERIALS AND METHODS

Nicosulfuron and thifensulfuron-methyl (technical grade, 98%) were both supplied from Institute for Plant Protection, Belgrade. The pure stock solution of chlorine dioxide (3 g L^{-1}) was prepared by mixing sodium chlorite (Superior Water Disinfection Power, TwinOxide®) and sodium bisulphate (Superior Water Disinfection Power, TwinOxide®), in 1 L of distilled water. The exact concentration of chlorine dioxide in the stock solution was quantified using 4500-ClO_2 DPD method according to the Standard Method [19]. Sodium-thiosulfate ($Na_2S_2O_3$, p.a., Merck) was used as received.

Acetonitrile (> 99.9%, Sigma-Aldrich HPLC grade), formic acid (Fluka analytical HPLC grade,) and water (HPLC grade water, Sigma-Aldrich) were used for HPLC analysis. Syringe filters (25 mm, PTFE membrane 0.45 μm) were obtained from Agilent Technologies.

In all experiments concentration of pesticides was 10 ppm. Pesticides were dissolved in acetonitrile and then were diluted using ultra-pure water to the desired concentration. Pesticide solutions were treated with a solution of chlorine dioxide (concentrations of 5 and 10 ppm). Samples were taken from reaction mixture after 30 min, 1 h, 2 h, 3 h, 6 h and 24 h of degradation, and the reaction is interrupted by degradation of a standard 0.1 mol dm^{-3} solution of $Na_2S_2O_3$ (in 10 mL of sample was added approximately 0.3 mL of a solution of $Na_2S_2O_3$). In order to optimize the conditions for degradation of pesticides, degradation was investigated in the dark and in the light, as well as at different pH values (3, 7 and 9). The pH values were adjusted with sulfuric acid (conc. 98%, Sigma-Aldrich) and sodium-hydroxide (analytical grade Sigma-Aldrich).

Degradation efficiency of pesticides was monitored using HPLC (Dionex Ultimate 3000, Thermo Fisher) with photodiode array detection on Hypersil Gold aQ C18 analytical column (150 mm x 3 mm, 3 µm) at 40 °C. Mobile phase consisted of 0.1% formic acid water solution as component A and acetonitrile as component B. The chromatographic elution was conducted at flow rate of 0.6 ml/min in gradient mode: 5 – 95% B in 8 min. Injection volume was 25 µl. Data analysis was performed with software Chromeleon, v6.8 (ThermoFisher Scientific, Bremen, Germany). At appropriate time intervals samples were taken from reaction mixture and quenched using $Na_2S_2O_3$. Degradation efficiency was calculated for each sample by the equation:

$$\eta = \frac{P_0 - P_t}{P_0} * 100$$

where η was degradation efficiency (%); P_0 was peak area of initial pesticide concentration; Pt (mAU⁄min) was peak area of residual pesticide concentration.

Acute toxicity tests with *Daphnia magna* were performed according to standardized guidelines OECD 202 [20] with temperature 21±1 °C and photoperiod of 16 h light/8 h dark. Five Daphnia magna neonates not older than 24 h were placed in each vessel with 25 ml of the tested medium (dilution medium was prepared according to the standard method ISO 6341). Acute toxicity tests were performed in borosilicate glasses with control and five test dilutions (6.25%, 12.5%, 25%, 50%, and 100%) with four replicates per dilution. Neonates were not fed during the exposure. Endpoint was the mortality of neonata. Toxic effect for each sample was expressed as the percentage of mortality. Tests were considered valid if the mortality in the control did not exceed 10 %. Immobilization of the neonates was observed after 24 and 48 h, and the results were compared to the control. The LC_{50} (lethal concentration which causes mortality of test organism by 50%) values with 95% confidence intervals were estimated by regression model: Spearman–Karber using TesTox software, version 1.0. We have analyzed the degradation products of herbicides after 24 h of treatment of chlorine dioxide.

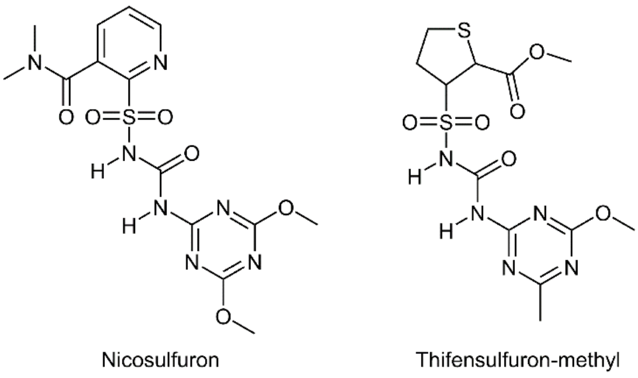

Figure 1. Chemical structure of the herbicides

RESULTS AND DISCUSSION

In view of the increasing usage of chlorine dioxide in water treatment it is important to investigate its reactivity with common organic contaminants, such as pesticides. Optimization of chlorine dioxide dosage, different time of degradation and at different pH values of solutions were performed in system with deionized water. Chlorine dioxide was added in deionized water solution of pesticide. Concentration of pesticide was 10 ppm.

The percentage of degradation was monitored by HPLC analysis on the basis of the pesticide peak area reduction after degradation compared to the peak area of the pesticides prior to degradation.

Analysis of nicosulfuron samples showed that at a concentration of 5 ppm ClO_2, high efficiency of degradation was not achieved in the dark or in the light (in the dark, after 24 h, 48.47%; in the light, after 24 h, 64.27%) (Figure 2. A), whereas at a concentration of 10 ppm ClO_2 good efficiency of degradation also wasn't achieved in the dark (64.92% after 24 h). However good degradation efficiency was achieved in the light (after 24 h, 89.03%) (Figure 2. A). The results showed that the best degradation efficiency of 92.89% was achieved after 6 h at pH=3, at a concentration of 5 ppm ClO_2, while at the same pH and at a concentration of 10 ppm ClO_2 slightly lower efficiency of the degradation was achieved (87.44%). On the other pH values, 7 and 9 and at a concentration of 5 ppm ClO_2, satisfactory degradation efficiency was not observed (at pH=7, after 24 h, 67.57%; at pH=9, after 24 h, 59.24%) (Figure 2. B), but at a concentration of 10 ppm ClO_2, at pH 7 and 9 somewhat higher degradation efficiency was achieved (at pH=7, after 24 h, 82.25%; at pH=9, after 24 h, 83.19%) (Figure 2. B). Degradation products analysis and their toxicity evaluation was done using NS sample with the best degradation efficiency, e.g. by treating NS sample with 5 ppm ClO_2 at pH=3 during 6 h.

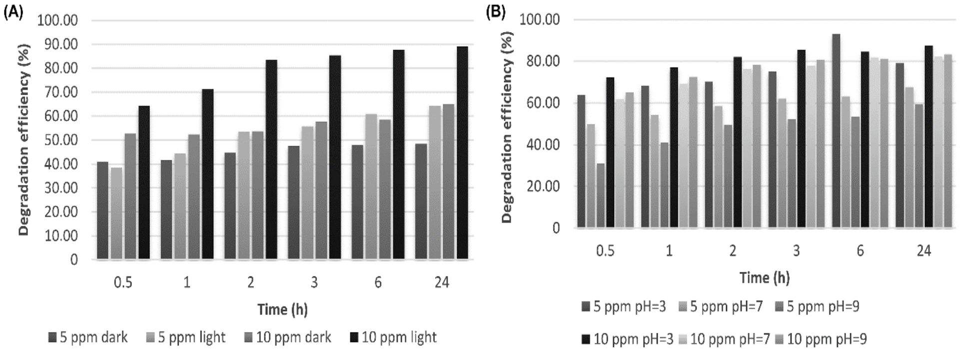

Figure 2. Degradation efficiency of nicosulfuron: at concentrations 5 and 10 ppm ClO_2 under light and dark (A) and at different pH values (B)

Analysis of TFSM samples showed that at a concentration of 5 ppm ClO_2 in the dark high efficiency of degradation was not achieved, while in the light at the same concentration of chlorine dioxide, somewhat better efficiency of degradation was achieved, but it was still not satisfactory (in the dark, after 24 h, 34.38%; in the light, after 24 h, 50.83%) (Figure 3. A). At a concentration of 10 ppm ClO_2 in the dark, efficiency of the degradation was not satisfactory, while in the light good degradation efficacy was achieved (in the dark, after 24 h, 46.75%; in the light, after 24 h, 73.18%) (Figure 3. A). Satisfactory degradation efficiency was not achieved at all observed pH values and at a concentration of 5 ppm ClO_2 (at pH=3, after 24 h, 55.86%; at pH=7, after 24 h, 36.96%; at pH=9, after 24 h, 46.29%) (Figure 3. B). However, at a concentration of 10 ppm ClO_2 and at all pH values relatively good degradation efficiency was achieved, but lower compared to degradation of TFSM with ClO_2 in the light (at pH=3, after 24 h, 67.23%; at pH=7, after 24 h, 61.36%; at pH=9, after 24 h, 67.26%) (Figure 3. B).

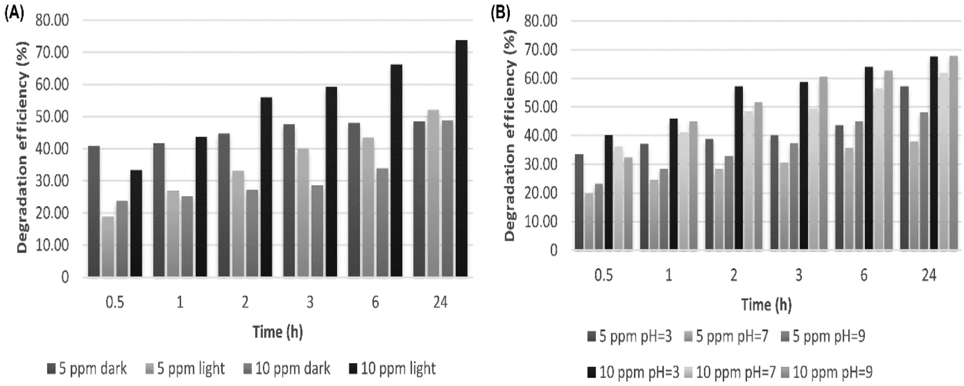

Figure 3. Degradation efficiency of thifensulfuron-methyl: at concentrations 5 and 10 ppm ClO_2 under light and dark (A) and at different pH values (B)

For analysis of degradation products and their toxicity, sample with best degradation efficiency was used, i.e. TFSM sample treated with 10 ppm ClO_2 after 24 h without pH value adjustment.

For the same samples ecotoxicological analysis was performed using *Daphnia Magna*. The data obtained indicate that degradation products of the NS sample, as well as TFSM sample have lower toxicity than the starting herbicides and may be classified in a category III (Toxic unit (TU) = 1-10; TU = 1/LC_{50}) (Table 1), as acute toxic on a scale from I to V [21].

Table 1. Results of toxicity of degradation products of the herbicides

Sample	LC_{50} (%, v/v) 48h
NS: 10 ppm NS + 5 ppm ClO_2 + pH=3 + 6 h	78.92
TFSM: 10 ppm TFSM + 10 ppm ClO_2 + light + 24 h	73.56

CONCLUSION

Degradation of sulfonylurea herbicides, nicosulfuron and thifensulfuron-methyl (10 ppm) was studied in deionized water under light and dark conditions with different dosage of chlorine dioxide, different time of degradation and at different pH values of solutions. It was found that the degradation of herbicides with chlorine dioxide happens in the dark and in the light and at all pH values. The most efficient degradation of TFSM was obtained in the light at a concentration of 10 ppm of ClO_2, and it was 73%, while in the case of NS the most effective degradation was achieved at concentration of 5 ppm of ClO_2 at a pH=3 and it was 93%. Toxicological analysis showed that the resulting degradation products of herbicides have lower toxicity compared to the starting herbicides and may be classified in a category III, as well as acute toxic on a scale of I to V. Further research will tend to reducing of toxicity.

Acknowledgements

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REFERENCES

1. Shukla G, Kumar A, Bhanti M, Joseph PE, Taneja A, Organochlorine pesticide contamination of ground water in the city of Hyderabad, *Environmental International* 32, 244–247 (2006).
2. Park J, Brown MT, Depuydt S, Kim JK, Won DS, Han T, Comparing the acute sensitivity of growth and photosynthetic endpoints in three Lemna species exposed to four herbicides, *Environmental Pollution* 220, 818-827 (2017).
3. Milne G. W. A, Handbook of pesticides, CRC Press LLC, Florida (1998).
4. Konstantinou IK, Hela DG, Albanis TA, The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels, *Environmental Pollution* 141, 555-570 (2006).

5. Davezza MD, Pramauro FE, Prevot AB, Photocatalytic degradation of bentazone in soil washing wastes containing alkylpolyoxyethylene surfactants, *Chemosphere* 86, 335–340 (2012).
6. Liu Z, Yan X, Drikas M, Zhou D, Wang D, Yang M, Qu J, Removal of bentazone from micro-polluted water using MIEX resin: Kinetics, equilibrium and mechanism, *Journal of Environmental Sciences* 23, 381–387 (2011).
7. Gonzalez JM, Ukrainczyk L, Adsorption and desorption of nicosulfuron in soils, *Journal of Environmental Quality* 25, 1186–1192 (1996).
8. Fan J, Wei Z, Ming ZZ, Xiang X, Jun WJ, Zhen Q, Ke L, Ming LL, Desorption character of nicosulfuron and effect of pH on adsorption of nicosulfuron in soils, *Southwest China Journal of Agricultural Science* 21, 702–708 (2008).
9. Ukrainczyk L, Rashid N, Irreversible sorption of nicosulfuron on clay minerals, *Journal of Agricultural and Food Chemistry* 43, 855–857 (1995).
10. Tian F, Qiang Z, Liu C, Zhang, T, Dong B, Kinetics and mechanism for methiocarb degradation by chlorine dioxide in aqueous solution, *Chemosphere* 79, 646–651 (2010).
11. Wang Y, Liu H, Liu G, Xie Y, Oxidation of diclofenac by aqueous chlorine dioxide: Identification of major disinfection byproducts and toxicity evaluation, *Science of the Total Environment* 473–474, 437–445 (2014).
12. Hörsing M, Kosjek T, Andersen HR, Heath E, Ledin A, Fate of citalopram during water treatment with O_3, ClO_2, UV and fenton oxidation, *Chemosphere* 89, 129–135 (2012).
13. Chen Q, Wang Y, Chen F, Zhang Y, Liao X, Chlorine dioxide treatment for the removal of pesticide residues on fresh lettuce and in aqueous solution, *Food Control* 40, 106-112 (2014).
14. Sharma VK, Oxidative transformations of environmental pharmaceuticals by Cl_2, ClO_2, O_3, and Fe (VI): Kinetics assessment, *Chemosphere* 73, 1379–1386 (2008).
15. Lopez A, Mascolo G, Tiravanti G, Passino R, Degradation of herbicides (ametryn and isoproturon) during water disinfection by means of two oxidants (hypochlorite and chlorine dioxide), *Water Science and Technology* 35, 129–130 (1997).
16. Tian F, Qiang Z, Liu C, Zhang T, Dong B, Kinetics and mechanism for methiocarb degradation by chlorine dioxide in aqueous solution, *Chemosphere* 79, 646–651 (2010).
17. Chen Q, Wang Y, Chen F, Zhang Y, Liao X, Chlorine dioxide treatment for the removal of pesticide residues on fresh lettuce and in aqueous solution, *Food Control* 40, 106-112 (2014).
18. Tian F-X, Xu B, Zhang T-Y, Gao N-Y, Degradation of phenylurea herbicides by chlorine dioxide and formation of disinfection by-products during subsequent chlor(am)ination, *Chemical Engineering Journal* 258, 210–217 (2014).
19. APHA (American Public Health Association), American Water Works Association, and Water Environment Federation. Standard Methods for the

Examination of Water and Wastewater, 20th ed. American Public Health Association, Washington DC (1998).

20. OECD Guideline for testing of chemicals. Daphnia sp. Acute Immobilisation Test. OECD Guideline 202 (2004).
21. Persoone G, Marsalek B, Blinova I, Törökne A, Zarina D, Manusadzianas L, Nalecz-Jawecki G, Tofan L, Stepanova N, Tothova L, Kolar B, A practical and user-friendly toxicity classification system with microbiotests for natural waters and wastewaters, *Environmental Toxicology* 18, 395-402 (2003).

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COSMETICS, SAFE OR NO?

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ABSTRACT

Cosmetics have been part of public thoughts since 4000 BC.

Nowadays, the use of hair colours, permanent make- up and eye lashes is in increase. Since number of substances has been considered as one of the cancer causes, risk evaluations have been done. Cosmetics Directive and after it Regulative, listed the substances that can be used in cosmetics, but with limitations. The newest thought of science committee defined 305 substances and certain warnings that has to be named within declaration.

Serbia should harmonized with the Legislative of EU.

Tattoos and permanent make- up are defined only by Resolution from 2008, which does not contain the use of rules named in Cosmetics Regulative.

Key words: Cosmetics, history, toxicology, health, declaration.

INTRODUCTION

Cosmetics history review

The first archaeological evidence of cosmetics use was found in Egypt 4000 BC. In that time women used to put light green pasta made from copper minerals in order to secure a color and a definition of the face. Eye make-up Egyptians used to make by mixing copper and lead, making the cream called mesdement. They used scented oils and cream made from lead, char and mutton tallow for eyebrows coloring. The canna was used as nail polish, and for lips and cheeks women used red clay mixed with water. Sugar syrup has been used for a depilation.

In Asia the rise powder was used as a make-up and the hair was dyed by canna.(1)

In Greece (1000BC), for the white face complexion people used a chalk or a lead powder 1(There was no evidence of lead poisoning in ancient Greece). When the women wanted to blush a little bit they mixed the ocher clay with the red grapes as a lipstick.(1)

In Rome (100BC) Platus wrote: Women without make-up is like a food without salt. Those civilized forebears used to put barley flour and butter to prevent acne's development and mutton tallow and blood for shiny nails. Their contribution when it comes to cosmetics was mud baths practice with crocodile's excrement for who knows which purpose. Men used to dye their hair in blue. They gave up on hair dying because the color was full of soda which cause the hair loss. They had specialized slaves which job was to use a cosmetics and they was called-pracosmetics. In 14th century the thought was that the make-up was damaging the health because it was stopping the circulation. In England (Elisabeth era) the most popular was red hair. Welfare women used to pale their faces complexion by using whites, they were sleeping with pieces of raw beef on their faces to prevent wrinkles. One English theatre writer said once- A beautiful woman is like delicacy.(1)

In Europe (15th to 16th century), only aristocracy used to use cosmetics. French population has perfected the creation of new scents and cosmetics, by mixing ingredients. Those processes present the beginning of modern cosmetics. But, sometimes those processes went wrong which even caused death. For example, instead of lead which is poising gradually, sometimes they used to put arsenic in powder which will immediately kill the one who is wearing it.

In 19th century French population has developed the chemical processes which have replaced perfumes made by natural processes. Zinc oxide became the replacement for deathly lead and copper, in powders. Other poisonous ingredients are still in use when it comes to lipsticks and eyeshadows.(1).

In 1990 The French chemist Eugene Schueller has developed first safe commercial hair color. Hair dying is ancient art. 3400 BC Egyptians used canna to cover the grey hair. Back in days, the color was extracted from plants and minerals. The development of synthetic colors was in 1800. when the existence of a substance called PPD (para-phenylenediamin) was revealed. In the same time was revealed that hydrogen peroxide is much better substance in comparison with others. These two major developments was the reason why the chemist Eugene Schueller was able to make the first commercial color called Aureole. This product is now known as L'Oreal.(1)

Today dying hair, eyebrows and eyelashes is the industry which considerably use both synthetic and colors made from plant's, clay's and land's pigments. Colors made from plant's, clay's and land's pigments could be contaminated with heavy metals, polycyclic hydrocarbons and other toxic substances which depends on which raw material's pigment were in use.

Today, most of the store-bought hair color options are made with harsh, toxic chemicals that can pose a serious health risk when used regularly over time.

MATERIAL AND METHOD

European cosmetics products regulations

In European Union cosmetic products were originally defined by Cosmetics directive 768/1976, with number of changes. Afterwards it was defined by Cosmetic products statute 1223/2009. The last change was made on 10th of February in 2017.
Cosmetics directive had 9 annexes in total.

ANNEX 1- illustrative list by category of cosmetic products
ANNEX 2 - list of substances which cosmetic products must not contain
ANNEX III PART 1 -List of substances which cosmetic products must not contain except subject to the restrictions and conditions laid down
PART 2- list of colouring agents which can be contained in cosmetics products intended to come into contact with the mucous membranes
ANNEX IV PART 1 list of substances provisionally allowed
PART 2 list of colouring agents provisionally allowed which may be contained in cosmetic products intended to come into contact with the mucous membranes in accordance with article 5
PART 3 (A) list of colouring agents provisionally allowed for cosmetic products which do not come into contact with the mucous membranes
ANNEX V list of substances excluded from the scope of the directive
Annex 5, 6 (changes 17. may 1982.)
ANNEX VI list of preservatives which cosmetic products may contain and part 1- list of preservatives allowed,
ANNEX VII List of UV filters which cosmetic products may contain, (changes 26. October 1983)

Regulation EU 1223/2009 have 8 Annex.
ANNEX I cosmetic product safety report (Part A – Cosmetic product safety information,
Part B – Cosmetic product safety assessment)
ANNEX II list of substances prohibited in cosmetic products
ANNEX III list of substances which cosmetic products must not contain except subject to the restrictions laid down (305 substances -2017.)
ANNEX IV list of colourants allowed in cosmetic products
ANNEX V list of preservatives allowed in cosmetic products
ANNEX VI list of uv filters allowed in cosmetic products
ANNEX VII symbols used on packaging/container
ANNEX VIII list of validated alternative methods to animal testing (3)

In this paper we would deal with the inset III, which contains substances that one cosmetic product can contain with certain limit as well as the lines about use and warnings which could be at the product declaration itself.

In the Directive 768/1976., in table in inset III was 29 substances. In the Statute 1223/2009 with all the changes up to now in inset III was 305 substances.

Toxicity

Today, most of the store-bought hair colour options are made with harsh, toxic chemicals that can pose a serious health risk when used regularly over time.

Some hair colour products can contain as many as 5,000 chemicals.

Some of the risks and side effects of the chemicals found in hair dyes include cancers of the kidney, bladder, and breast as well as blood-based cancers like leukemia and lymphoma.

One of the common chemicals used called p-Phenylenediamin (PPD) is documented as causing side effects like asthma, gastritis, severe dermatitis, eye irritation, vertigo, tremors, convulsions, kidney failure, and coma in those who are exposed to it. Some hair colour products include substances like lead acetate and ammonia. The chemicals in hair colour products also interact with the substances in human hair to produce harmful effects.

Hair colours come in temporary, semi-permanent and permanent solutions. However, 80 percent of the market is comprised of permanent colours which contain agents like couplers and intermediates that react with the hydrogen peroxide. While the worst hair colour product ingredients were banned in the 1970s, many products still contain dangerous substances.

Numerous studies have substantiated these hair colour risks.

A 1994 National Cancer Institute report covered the dangers of dark hair dyes used over extended periods of time. They were found to raise the risk of cancers like multiple myeloma and non-Hodgkin's lymphoma. Another study by the *International Agency for Research on Cancer* (IARC) found that hairdressers who worked regularly with these products had an increased risk of bladder cancer, leukemia and lymphoma.

The scalp area is very rich in its blood supply, making it all too easy for the toxic chemicals found in hair dyes to soak into the skin. During the 30 minutes that hair dyes remain in contact with the scalp, they can easily enter the blood supply. (4)

RESULTS

Potential risk from hair dyes

Following the publication of a scientific study in 2001, entitled 'Use of permanent hair dyes and bladder cancer risk', the Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers, subsequently replaced by the Scientific Committee on Consumer Products ('SCCP'), pursuant to Commission Decision 2004/210/EC of 3 March 2004 setting up Scientific Committees in the field of consumer safety, public health and the environment, concluded that the potential risks of the use of hair dyes were of concern. The SCCP, in its opinions, recommended that the Commission take further steps to control the use of hair dye substances.(3)

As regards the evaluation of possible consumer health risks by reaction products formed by oxidative hair dye substances during the hair dyeing process, based on the data yet available, the SCCS, in its opinion of 21 September 2010, did not raise any major concern regarding genotoxicity and carcinogenicity of hair dyes and their reaction products currently used in the Union.

In order to ensure the safety of hair dye products for human health, it is appropriate to set up maximum concentrations of ten assessed hair dye substances by taking into account the final opinions given by the SCCS on their safety.

The definition of a hair product in Regulation (EC) No 1223/2009 excluded the application of hair dye substances on eyelashes. That exclusion was motivated by the fact that the level of risk is different when cosmetic products are applied on the hair on the head and on eyelashes respectively. A specific safety assessment was therefore needed for the application of hair dye substances on eyelashes .(3)

The SCCS, in its opinion on oxidative hair dye substances and hydrogen peroxide used in products to colour eyelashes of 25 March 2015 (SCCS/1553/15), concluded that oxidative hair dye substances Toluene-2,5-Diamine, p-Aminophenol, 2-Methylresorcinol, Tetraaminopyrimidine Sulfate, Hydroxyethyl-p-Phenylenediamine Sulfate and 2-Amino-3-Hydroxypyridine, listed in Annex III to Regulation (EC) No 1223/2009 and found safe for use in hair dye products, can be safely used by professionals in products intended for colouring eyelashes. (3)

On the basis of the scientific assessment of those substances, their use should be allowed in products intended for colouring eyelashes. However, in order to avoid any risk connected with the self-application of products intended for colouring eyelashes by consumers, they should be allowed for professional use only. In order to allow professionals to inform consumers about possible adverse effects of the application of products intended for colouring eyelashes and to lower the risk of skin sensitivity to those products, appropriate warnings should be printed on their labels.(3)

Table 1. Some Restrictions and warnings from declaration

Restrictions			**Wordings of conditions of use and warnings**
Product type, body parts	Maximum concentration in ready use preparation	Other	
Hair dye substance in oxidative hair dye products		As from 3 September 2017, after mixing under oxidative conditions the maximum concentration applied to hair must not exceed 1,0 % - Do not use with nitrosating agents - Maximum nitrosamine content: 50 µg/kg - Keep in nitrite-free containers	As from 3 March 2018, to be printed on the label: The mixing ratio. " Hair colourants can cause severe allergic reactions. Read and follow instructions. This product is not intended for use on persons under the age of 16. Temporary 'black henna' tattoos may increase your risk of allergy. Do not colour your hair if: - you have a rash on your face or sensitive, irritated and damaged scalp, - you have ever experienced any reaction after colouring your hair, - you have experienced a reaction to a temporary 'black henna' tattoo in the past".
(a) Hair dye substance in oxidative hair dye products		(a) After mixing under oxidative conditions the maximum concentration applied to hair must not exceed 1,8 %	a) To be printed on the label: The mixing ratio. " Hair colourants can cause severe allergic reactions. Read and follow instructions. This product is not intended for use on persons under the age of 16. Temporary 'black henna' tattoos may increase your

b) Hair dye substance in nonoxidative hair dye products	(b) 1,8 %		risk of allergy. Do not colour your hair if: - you have a rash on your face or sensitive, irritated and damaged scalp, - you have ever experienced any reaction after colouring your hair, - you have experienced a reaction to a temporary ‘black henna’ tattoo in the past.”
(c) Products intended for colouring eyelashes		(c) After mixing under oxidative conditions the maximum concentration applied to eyelashes must not exceed 1,25 % (c) Professional use	(c) As from 3 March 2018, to be printed on the label: The mixing ratio. “ This product can cause severe allergic reactions. Read and follow instructions. This product is not intended for use on persons under the age of 16. Temporary ‘black henna’ tattoos may increase the risk of allergy. Eyelashes shall not be coloured if the consumer: -has a rash on the face or sensitive, irritated and damaged scalp, - has experienced any reaction after colouring hair or eyelashes, - has experienced a reaction to a temporary ‘black henna’ tattoo in the past. For professional use only. Rinse eyes immediately if product comes into contact with them”.’

Tattoos and permanent make-up use is in increase these days (12% of the whole European population has one tattoo or more), therefore it is important to include it to the law. (5)

In mentioned warnings was specified the warning for those who were already had one or more tattoos. Tattoos and colours for permanent make-up was not mentioned in the inset of the Statute, because there are not officialy part of cosmetic products. Tattoos and permanent make-up colour safety are defined in Resap resolution in 2008(6). We would mention only the part which is related to substances that are the part of tattoos and permanent make-up structure.

Tattoo and PMU products must only be used if they comply with all the following requirements:

- they do not contain or release the aromatic amines listed in Table 1 of the appendix. in concentrations that are technically avoidable according to good manufacturing procedures;
- they do not contain the substances listed in Table 2 of the appendix;
- they do not contain substances listed in Directive 76/768/EEC (Annex II);

- they do not contain substances specified in Directive 76/768/EEC (Annex IV, columns 2 to 4);
- they do not contain carcinogenic, mutagenic and reprotoxic substances of categories 1, 2 or 3 which are classified under Directive 67/548/EEC;
- they comply with maximum allowed concentrations of impurities listed in Table 3 and the minimum requirements for further organic impurities for colourants used in foodstuffs and cosmetic products as set out in Directive 95/45/EEC;(6)

In mentioned warnings was specified the warning for those who were already had one or more tattoos. Tattoos and colours for permanent make-up was not mentioned in the inset of the Statute, because there are not officialy part of cosmetic products. Tattoos and permanent make-up colour safety are defined in Resap resolution in 2008(6). We would mention only the part which is related to substances that are the part of tattoos and permanent make-up structure.

CONCLUSION

Following the literature and newest scientific knowledge we could make a conclusion that there is even larger number of substances used in cosmetic products production, but also that the risk assessments are regularly checked.

As much as the risk assessments are important, the warnings also have to be available to both professionals and customers. It is important that the list of those substances is updated.

In Serbia is still in use the Act on conditions concerning consumer goods safety attended for the market (Official Gazette SFRJ No. 26/83… 18/91). Nowadays the Act is in process of production, this Act should be in harmony with the Legislative of European Union about cosmetic products, therefore all the rules mentioned in Acts would be in use in our country too. Health safeness of tattoos and permanent make-up is still defined only by Resap Resolution (2008)1.

REFERENCES

1. Nikolovski A.(2009), Parfimerijski i kozmetički proizvodi, neobjavljen seminarski rad realizovan u okviru departmana na Tehničkom fakultetu u Boru, Univerziteta u Beogradu.
2. Official Journal of the European Communities, No L 262/169, COUNCIL DIRECTIVE of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products (76/768/EEC)
3. Official Journal of the European Communities, 11.2.2017, COMMISSION REGULATION (EU) 2017/237 of 10 February 2017 amending Annex III to Regulation (EC) No 1223/2009 of the European Parliament and of the Council on cosmetic products (Text with EEA relevance)

4. Schmidt D.Hair color warning: The clear link between hair coloring chemicals and cancer Dangerous Chemicals December 4, 2016
5. Piccinini P., Pakalin S., Contor L., Bianchi I., Senaldi C. Safety of tattoos and permanent make-up Final report, Administrative Arrangement N. 2014-33617 Analysis conducted on behalf of DG JUST,2016
6. Resolution ResAP(2008)1 on requirements and criteria for the safety of tattoos and permanent make-up (superseding Resolution ResAP(2003)2 on tattoos and permanent make-up) *(Adopted by the Committee of Ministers on 20 February 2008*

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RADIONUCLIDE CONTENT IN PREMIXES IN 2015 AND 2016

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ABSTRACT

As part of monitoring radionuclides in animal feed produced in the Republic of Serbia in 2015 and 2016, the gamma spectroscopy method was used to analyze 35 premix samples. In all analyzed samples activity levels of ^{137}Cs, were within the detection limits of the gamma spectroscopic device to 2.8 Bq/kg. From the viewpoint of the content of the analyzed radionuclides in animal premixed activity levels (Bq/kg) were: ^{137}Cs < 0.2 to 2.8 Bq/kg, ^{40}K from 11 to 502 Bq/kg, ^{226}Ra from 2.9 to 49 Bq/kg, ^{232}Th < 1.0 to 13 Bq/kg, and ^{238}U < 3.2 to 111 Bq/kg.

Key words: animal feed, premix, radionuclides.

INTRODUCTION

Ionization radiation has accompanied the living world since its formation and it is one of the characteristics of the environment. Radionuclides released into nature through different mechanisms enter the human organism from air, water and food and contribute to human irradiation. Based on systematic measurements of natural radionuclides in the soil, food, animal food, air and water different amounts of radionuclides can be registered in them that through food enter the organism of an inhabitant of a certain area.

Cosmic and terrestrial (primordal) radionuclides are natural sources of radionuclides. Cosmic radiation is a type of natural ionization radiation of the earth surface from the cosmos. Terrestrial radionuclides have a half-life comparable with the age of the Earth (4.5×10^9 years) or longer and have been created by nucleosynthesis at the same time as all substances of the Solar system [1,2].

Most radionuclides that exist on Earth can be grouped into three natural radioactive series. They are the uranium-radium series, uranium-actinium series and the thorium series. A fourth neptunium series was created in laboratory conditions by nuclear reactions. Natural radioactive series are created by the breakdown of three radioisotopes ^{235}U, ^{238}U and ^{232}Th that are still present in nature due to their long half-life. Descendants of these isotopes are also unstable so they break down forming new unstable lighter cores, with a stable isotope ending the series. Levels of natural radioactivity at some point on Earth depend on several factors: content of natural radioactive elements in the biosphere, type of cosmic radiation, geological characteristics of the soil, altitude, geographic latitude and longitude. Natural radioactivity levels differ on the Earth from place to place.

Potassium has three isotopes of which only ^{40}K emits radioactive radiation. Potassium-40 is an essential natural radionuclide that is part of the human organism. Depending on the chemical content of the soil, its structure, pH and moisture, radionuclides bond in the soil, and transfer from soil to plants. The ^{40}K radionuclide has a physical half-life ($T_{1/2}$) of 1.25×10^9 years and a biological half-life in the human body (T_b) of 58 days and represents 0.117% of natural potassium[3].

In nature uranium occurs as a mixture of three long-life isotopes: ^{238}U with $T_{1/2}$= 4.5×10^9 years and representation of 99.28%; ^{235}U with $T_{1/2}=7.1\times10^8$ years and representation of 0.71% and ^{234}U with $T_{1/2}=2.5\times10^5$ years and representation of 0.006%. All natural uranium isotopes dominantly emit alpha particles and their descendants are beta and/or gamma emitters. Regardless of its chemical form and time of acute exposure uranium in an organism acts as a toxicant as it acts as a source of ionization radiation and can also act as a chemically toxic element. The biological half-life of ^{238}U is between 1 and 500 days depending on the mobility of uranium compounds[3].

Radium is a natural radioactive element that has four isotopes of which ^{226}Ra and ^{228}Ra are the products of radioactive breakdown of uranium. Due to a physical half-life of 1600 years, high chemical activity, low degree of elimination from an organism (T_b=7-45 years) its amount in an organism increases with time. In an organism it follows calcium and is one of the more toxic radionuclides with an extremely expressed cancerous action [1,2].

Thorium isotopes: ^{232}Th with a half-life of 1.4×10^{10} years and ^{228}Th with a half-life of 1.9 years have radio-ecological significance[1]. ^{232}Th is the most significant member of the thorium series of radioactive breakdown. Bones, lungs and liver are its main deposition points.

Two of seven radioactive isotopes of cesium are significant for environment pollution: ^{134}Cs ($T_{1/2}$ = 2.06 years) and ^{137}Cs ($T_{1/2}$ =30.17 years). Both radionuclides were present in fuel elements of the nuclear reactor in Chernobyl (1986) from where they were emitted into the environment. Radiocesium most often reaches plants by dry or wet precipitation. The cesium ion is a chemical and biochemical homologue of potassium and follows its metabolism in an organism. It can be ingested by physical or chemical sorption or ion exchange. It is completely soluble in body fluids and is uniformly distributed in the organism. Due to this property there is no critical organ for cesium and it is an organothropic radionuclide. Its physico-chemical characteristics are such that it actively enters the human and animal food chain through plants. The ^{137}Cs anthropogene radionuclide to the greatest extent entered the environment in Serbia after the accident in the Chernobyl nuclear power plant in the Ukraine in 1986. There were no significant deposits of this radionuclide in Serbia after the accident in the Fukushima nuclear power plant in Japan in 2011[4].

Modern biotechnical production represents a very complex food chain starting from plant production and a series of agrotechnical measures for advancing this production, through livestock production. This food chain ends with final biotechnical products – plant and animal food with man as its basic and most significant consumer[5]. Radionuclides originating from the soil, water and air can enter the food chain by deposition and/or migration. They enter soil and water by migration and collection and via them into plant and animal food.

Internal exposure of animals to radionuclides can occur through skin, inhalation and ingestion. Ingestion is the most common way radionuclides enter an animal organism. The danger of exposing livestock production to radioactive contamination results from the fact that radionuclides migrate very fast in the livestock production cycle. A whole series of factors exist that hamper possible interruption of the transfer of radionuclides in the food chain from animals and their products to man.

High production with minimal production costs are the requirements of modern livestock production. In order to realize this it is necessary to adapt nutrition according to amount and type to a species and category of animal. According to the Rules of Animal Food Quality it follows that animal food is any substance or product that is unrefined or has been partially refined and is intended for feeding animals used for food production in the form of: feed, premix and mixture[6]. Suitable animal feeding is one of the most important conditions for proper growth, development and health of animals and must be adjusted to each animal species and current metabolic needs. Nutrition should give an animal all necessary nutrients in accordance to its physiological state. This to the greatest degree depends on the category, animal age and life cycle phase. Adequate nutrition improves animal health, increases consumption and efficiency of food utilization, changes certain physiological processes in the animal organism and thus stimulates its growth and improves the quality of obtained products. The need for proteins and energy are the highest, but a deficit of only one vitamin or mineral in a feed causes specific disorders leading to deterioration of the animals general state and reduced production. Over 30 nutrients in a suitable amount and ratio need to be provided in animal feed. In order to reach optimum different premixes and additives are added to nutrients. Vitamins, minerals, essential amino-acids, saturated fats, different probiotics and prebiotics are most often added[7-9].

Premixes are products with high content of vitamins, amino-acids and allowed additives that are homogeneously mixed with a carrier. They are used for animal feed combined with nutrients or for making mixtures. Premixes can be:

- *mineral* (contain a mixture of allowed minerals that have no energy value for the organism but are significant as gradient elements in different activities and biological systems as they perform many vital functions in the organism),
- *vitamin* (contain only vitamins – complex organic compounds, physiologically active that regulate the metabolism of matter in the organism. The organism

does not synthesize them or synthesizes them in insufficient amounts that require their substitution through food or vitamin additives. Each individual vitamin has a specific role in the organism that cannot be replaced by any other form of chemical compound),

- *vitamin-mineral* (contains allowed minerals and vitamins) and
- *other premixes* (these are premixes with amino-acids, premixes of non-protein nitrogen compounds).[6]

MATERIAL AND METHODS

Samples of premixes for animals were collected in 2015 and 2016 on the territory of the Republic of Serbia in factories for animal food production, factories for mineral nutrient production, on farms, in retail (agriculture pharmacies) and obtained from individual producers.

In 2015 16 premix samples were collected for monitoring, while in 2016 there were 19 samples.

After delivery to the laboratory, the samples were homogenized and packed in Marinelli vessels with a volume of 1 L sealed with paraffin and left to sit for at least four weeks to establish a radioactive balance between ^{226}Ra, ^{222}Rn and their short-life products. Gamma-spectrometric measurements of samples of animal feed were performed using the standard method of the International Agency for Atomic Energy[9,10]. A semiconducting germanium detector with a high purity of the n type produced by ORTEC - AMETEK, USA, with 8192 channels, resolution 1.65 keV and relative efficiency of 34% at 1.33 MeV for ^{60}Co was used for determining radionuclide activity levels. Calibration of the detector energy and efficiency was performed by the Department of Physics, Faculty of Natural Sciences, University of Novi Sad. All samples were measured at 14400 s. Spectrum analysis was performed using the Gamma Vision 32 program[11]. Activity levels of ^{238}U were determined using gamma lines: ^{234}Th (63 and 93 keV) and ^{234}Pa (1001 keV). Activity levels of ^{226}Ra were determined using gamma lines: ^{214}Bi (609, 1120 and 1764 keV) and ^{214}Pb (295 and 352 keV). Activity levels of ^{232}Th were determined using gamma lines ^{228}Ac (338, 911 and 969 keV). Activity levels of ^{40}K were determined using gamma lines at 1460 keV, and for ^{137}Cs gamma lines at 661.6 keV.

In order to secure checks of the measuring device for potential pollution periodical measurement of the background radiation of the detector system was performed. Background radiation measurement was performed just before sample measurement. Minimal detectable levels of radionuclide activity (Bq/kg) were determined using the Currie equation[12]. The relative measuring uncertainty of all results was up to 10% of the activity levels of analyzed samples. Quality control of gamma spectroscopic measurements, based on which investigated samples were analyzed, was performed using a calibration standard and reference materials and regular yearly participation in evaluations between laboratories organized by the International Agency for Atomic Energy.

MEASUREMENT RESULTS AND DISCUSSION

Tables 1 and 2 show minimal and maximal values of activity levels of natural (^{226}Ra, ^{232}Th and ^{238}U) and artificially produced radionuclides ^{137}Cs (Bq/kg) and the number of premixes.

For monitoring purposes in 2015, 16 premix samples were collected used in nutrition of: cattle (2 samples), pigs (4 samples), poultry (8 samples), lambs (1 sample) and all animal species (1 sample). For monitoring purposes in 2016 19 premix samples were collected that were used in nutrition: cattle (4 samples), pigs (8 samples), poultry (6 samples) and all animal species (1 sample).

Table 1. Activity levels of ^{137}Cs, ^{40}K, ^{226}Ra, ^{232}Th and ^{238}U (Bq/kg) in premixes collected in 2015

Sample name (sample number)	**^{137}Cs**	**^{40}K**	**^{226}Ra**	**^{232}Th**	**^{238}U**
	(Bq/kg)				
Premix for beef cattle (1)	< 0.2	104	2.9	1.5	< 3.2
Premix for cows (1)	< 0.3	143	8.1	1.9	< 5.1
Premix for pigs (1)	< 0.2	64	6.5	2.2	< 3.6
Premix for fattening pigs (2)	< 0.2	96; 351	< 4.7	< 1.0	< 4.3
Premix for sows (1)	< 0.2	142	4.9	1.7	< 4.2
Premix for chicken (3)	< 0.2	25 - 78	< 4.1	< 1.0 - 2.5	< 4.3
Premikx for laying hens (5)	< 0.3	29 - 98	3.4 - 49	< 1.0 - 2.3	< 3.7 - 100
Premix for lambs (1)	< 0.2	130	4.4	< 1.0	< 3.5
Premix for all animals (1)	< 0.2	75	8.0	2.3	8.6

Table 2. Activity levels of ^{137}Cs, ^{40}K, ^{226}Ra, ^{232}Th and ^{238}U (Bq/kg) in premixes collected in 2016

Sample name (sample number)	**^{137}Cs**	**^{40}K**	**^{226}Ra**	**^{232}Th**	**^{238}U**
	(Bq/kg)				
Premix for beef cattle (2)	< 0.3	30; 71	6.9; 7.2	< 1.0; 2.3	< 4.7
Premix for cows (2)	< 0.2	11; 26	7.8; 9.1	1.6; 1.7	8.8; 9.4
Premix for piglets (2)	< 0.4	119; 153	< 7.8	< 1.5; 6.9	< 7.6
Premix for pigs (4)	< 0.2 - 2.8	15 - 502	3.2 - 44	< 1.0 - 13	< 3.9 - 111
Premix for sows (2)	< 0.3	27; 117	6.7; 9.2	< 1.0; 1.4	< 3.8; 10
Premix for chicken (4)	< 0.3	36; 61	6.5; 7.8	< 1.0; 3.9	< 7.1
Premix for laying hens (2)	< 0.3	25 - 111	< 4.1 - 46	< 1.0 - 1.6	< 3.7 - 103
Premix for all animals (1)	< 0.2	22	8.3	< 1.0	19

The results given in Table 1 indicate that activity levels of ^{137}Cs in premix samples from 2015 were < 0.3 Bq/kg, ^{40}K from 25 to 351 Bq/kg, ^{226}Ra from 2.9 to 49 Bq/kg, ^{232}Th < 1.0 to 2.5 Bq/kg, and ^{238}U < 3.2 Bq/kg to 100 Bq/kg.

The results given in Table 2 indicate that activity levels of ^{137}Cs in premix samples in 2016 < 0.2 to 2.8 Bq/kg, ^{40}K from 11 to 502 Bq/kg, ^{226}Ra from 3.2 to 46 Bq/kg, ^{232}Th < 1.0 to 13 Bq/kg, and ^{238}U < 3.7 to 111 Bq/kg.

Research from 2011[13] show that activity levels of radionuclides in piglet premix (Bq/kg) on the territory of Serbia were for ^{137}Cs < 0.1; < 0.2, ^{40}K 25; 220; ^{238}U < 4.0; 9.6 and ^{226}Ra < 2 to 4.2, in pig premix (Bq/kg) ^{137}Cs < 0.1 to < 0.5, ^{40}K from 31 to 511, ^{238}U < 4.0 to 25 and ^{226}Ra < 2 to 12, in premix for fattening pigs (Bq/kg) ^{137}Cs < 0.1, ^{40}K from 73 to 79, ^{238}U 11 to 507 i ^{226}Ra 1.2 to 111.

Activity levels in premixes from Denmark, Germany and France were for ^{137}Cs < 0.3 to < 0.5 Bq/kg, ^{40}K from 17 to 62 Bq/kg, ^{238}U from< 9 to 718 Bq/kg and ^{226}Ra from < 01 to 326 Bq/kg. Sparse research on the influence of radionuclides on animals warn that animals are chronically contaminated with uranium, as intake of this radionuclide by the animal starts in the earliest period and ends with its slaughter. Also, the degree of the transfer of radionuclides from the digestive tract into the meat depends on the animal species. The calculated transfer coefficient indicates the fact that poultry meat can present a potential danger for human consumption[15].

CONCLUSION

In order to obtain safe and secure food for human consumption monitoring of animal feed samples on the territory of Serbia is necessary.

As part of monitoring radionuclides in animal feed produced in the Republic of Serbia in 2015 and 2016, the gamma spectroscopy method was used to analyze 35 premix samples. In all analyzed samples activity levels of ^{137}Cs, were within the detection limits of the gamma spectroscopic device to 2.8 Bq/kg, indicating that animal feed produced in the Republic of Serbia is not contaminated with this artificially produced radionuclide.

From the viewpoint of the content of the analyzed radionuclides in animal premixed activity levels (Bq/kg) were: ^{137}Cs < 0.2 to 2.8 Bq/kg, ^{40}K from 11 to 502 Bq/kg, ^{226}Ra from 2.9 to 49 Bq/kg, ^{232}Th < 1.0 to 13 Bq/kg, and ^{238}U < 3.2 to 111 Bq/kg.

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REFERENCES

1. Kathren R.L., Radioactivity in the Environment: Sources, Distribution and Surveillance, Harwood Academic Publishers, Amsterdam, 1984.
2. Peterson R.S., Experimental γ Ray Spectroscopy and Investigations of Environmental Radioactivity, Spectrum Tehniquies, USA, 1996.
3. Dangić A., Geohemijski procesi u prirodi i radionuklidi, Jonizujuća zračenja u prirodi (monografija), Jugoslovensko društvo za zaštitu od zračenja, Beograd, 1995, 41-56.

4. Bikit I., Mrđa D., Todorović N., Nikolov J., Krmar M., Vesković M., Slivka J., Hansman J., Forkapić S., Jovančević N., Airborne radioiodine in northern Serbia from Fukushima, J Environ Radioact, 2012, 114, 89-93.
5. Marković J., Istraživanja parametara životne sredine i analiza uticaja na kvalitet prinosa, doktorska disertacija, Univerzitet Union-Nikola Tesla, Beograd, Fakultet za ekologiju i zaštitu životne sredine, Beograd, 2016.
6. Pravilnik o kvalitetu hrane za životinje, Službeni glasnik Republike Srbije, 4/2010, 113/2012 i 27/2014.
7. Kovčin S., Ishrana svinja, Poljoprivredni fakultet, Novi Sad, 1993.
8. National Research Council Nutrient requirments of poultry, ninth revised edition, National Academy Press, Washington, D.C., 1994.
9. Arruda-Neto J.D.T., Tavares M.V., Filadelfo M., Concentracion of uranium in animal feed suplements: measurements and dose estimates, J Radioanal Nucl Chem, 1997, 221, 97-104.
10. Measurement of Radionuclides in Food and Environment, A Guidebook, Technical Report series No. 295, IAEA, Vienna, 1989.
11. ORTEC, Gamma Vision 32, Gamma – Ray Spectrum Analysis and MCA Emulation, ORTEC, Oak Ridge, Version 5.3., 2001.
12. Currie L.A., Nomenclature in evaluation of analytical methods including detection and quantification capabilities, Pure Appl Chem, 1995, 67, 1699-1723.
13. Mitrović R., Kljajić R., Petrović B., Vuković D., Rezultati analize radioaktivnog cezijuma (^{134,137}Cs) u biotehničkoj proizvodnji za period 1985-1995. godina, Zbornik radova, Savetovanje Černobilj, 10 godina posle, Jugoslovensko društvo za zaštitu od zračenja, Budva, jun 1996, Beograd, 1996, 123-126.
14. Vitorović G., Mitrović B., Vitorović D., Andrić V., Adamović I., Radiation hygienic control of mineral supplements and feed for pigs, Biotechnology in Animal Husbandry 27(3), 835-842, 2011.
15. Handbook of parameter values for the prediction of radionuclide transfer in temperate environmenta, IAEA,Technical reports series No. 364, Vienna, 1994.

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POLLUTANT TRANSPORT IN WATERS AND THEIR PROCESSES

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ABSTRACT

The fate of pollutants in waters is controlled by physical transport and biogeochemical interactions in the system. The understanding of these interactions is critical step in predicting the fate of substances in water bodies.

Water quality models can be applied to many different types of water system, including streams, rivers, lakes, reservoirs, estuaries, coastal waters and oceans. The models describe the main water quality processes, and typically require the hydrological and constituent inputs (the water flows or volumes and the pollutant loadings). These models include terms for dispersive and/or advection transport depending on the hydrological and hydrodynamic characteristics of the water body, and terms for the biological, chemical and physical reactions among constituents.

Advection transport dominates in rivers. Dispersion is the predominant transport phenomenon in estuaries subject to tidal action. Lake-water quality prediction is complicated by the influence of random wind directions and velocities that often affect surface mixing, currents and stratification.

In coastal waters and oceans, large-scale flow patterns and tide are the most important transport mechanisms.

The development and application of water quality models is both a science and an art. Each model reflects the creativity of its developer, the particular water quality management problems and issues being addressed, the available data for model parameter calibration and verification, the time available for modeling and associated uncertainty, and other considerations. The fact that most, if not all, water quality models cannot accurately predict what actually happens does not detract from their value. Even relatively simple models can help managers understand the real world prototype and estimate at least the relative, if not actual, change in water quality associated with given changes in the inputs resulting from management policies or practices.

Key words: transport, advection, dispersive, diffusion, convection, pollutant.

INTRODUCTION

A process of mass transport is the process of moving chemical substances and other fluid characteristics in the environment where chemical susceptibilities are present [13] [14]. In the process of transporting pollutants most interest represents the distribution of polluting substances in the water bodies. Pollutants after passing through river waters or lakes behave differently: some are dissolved and are displaced by water currents, others are discharged from solid particles into the sediment and sediments and others can enter in biochemical cycles varying from one organism to another.

Dissemination of polluting substances in aquatic environments is carried out through the same mechanisms that cause the diffusion of polluting substances into the atmosphere, such as diffusion, molecular diffusion, turbulent diffusion, dispersion (Figure 1) and advection / convection.

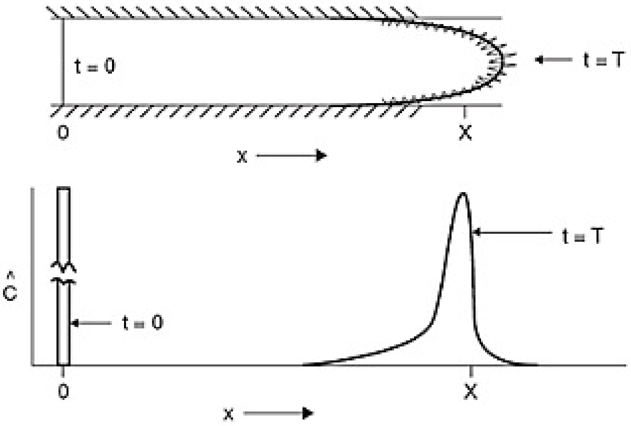


Figure 1. Dispersion
The longitudinal dispersion illustration in a "plane" for t = 0 in "stain" distributed at t = T° C is the indirect section of the mean concentration value.

Among the most important mechanisms that influence the distribution of pollutants in aquatic environments, we mention [1] [5]: Convection currents caused by significant water mass movements and diffusion due to occasional movements, which are the cause of exchanges of polluting substances in the vicinity. Transportation of dissolved substance is carried out from left to right; Movement of the dissolved substances is carried out through the concentration gradient (dC / dx). (Figure 2).

The combined effect of these factors is known as dispersion of pollutants into the aquatic environment (Figure 3).

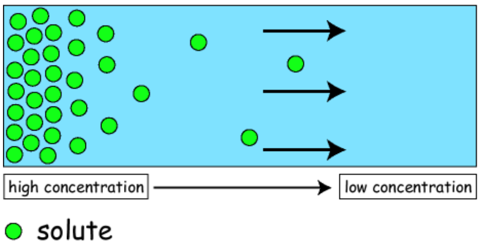


Figure 2.
Diffusion process

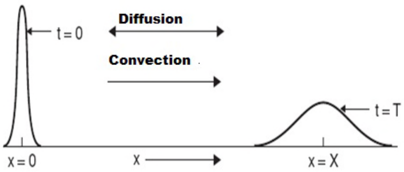


Figure 3.
Convection and Diffusion of a chemical substance stain along axis x.

The deterioration of water quality due to emissions of pollutants is evidently manifested in rivers, unlike the seas and oceans, which are considered to have an endless capacity for the elimination of pollution [4] [8] [17].

Examples of other processes are:

Biochemical interaction such as ammonium and oxygen in the formation of nitrites;

Growth of algae (primary production);

Chemical reactions;

Many of the reactions affect the growth or decrease of the concentrations of the constituents, they are usually presented by first-order kinetics that receive reaction rates and are proportional to the concentration of the constituents. While high-order kinetics may be accurate in certain situations, constituent concentrations of constituents based on first-order kinetics are usually acceptable for natural water systems [3] [5] [13].

In order to evaluate the spread of chemical, organic, inorganic or mineral contaminants dissolved in a water environment, it is imperative to provide methods based on mathematical models of diffusion-convection transport. To describe the transport processes, the diffusion and convection mechanisms must be considered, and this is done by solving and using the convection - diffusion equation [20] [21].

MATHEMATICAL FORMULATION. DIFFUSION-CONVECTION EQUATION

The convection diffusion equation is a parabolic equation of partial differences that describes the physical phenomena in which particles (particles) or energy (or other physical quantities) are transferred within the physical system through two processes: diffusion and convection. In its simplest form (when the diffusion coefficient and convection speed are constant and when there are no sources or pits) the equation takes the form [18] [19]:

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \vec{v} \cdot \nabla c \tag{1}$$

The two terms on the right side represent different physical processes, the first corresponds to the diffusion, second describes the convection or the advective which is the equation also known as the diffusion-diffusion equation. Further, c is the variable of interest (the concentration of species for mass transport, T for heat transfer), the constant D is the diffusion for the species or heat transfer, and is the vector of velocity.

The equation of Convection – diffusion in R^2 is written in the form [3]:

$$\frac{\partial \phi}{\partial t} = -u_x \frac{\partial \phi}{\partial x} - u_y \frac{\partial \phi}{\partial y} + D_x \frac{\partial^2 \phi}{\partial x^2} + D_y \frac{\partial^2 \phi}{\partial y^2} + \mathrm{q} \tag{2}$$

where:
(x,y) – coordinates in x and y axes;
T – time;
Φ – Concentration, Φ = Φ (x,y,t);
q – resorcue density;
U – Component speed vector u_x and u_y, rrespectively according to coordinating axes 0X and 0Y;

D – Diffusion coefficient tensor, $D = \begin{Vmatrix} D_x & 0 \\ 0 & D_y \end{Vmatrix}$, where D_x and D_y are the main components respectively according to 0X and 0Y.

In the particular case, when the problem is settled and the source density is q = 0 then:

$\phi = \phi(x, y)$, $\frac{\partial \phi}{\partial t} = 0$, and the equation (11) takes the form:

$$D_x \frac{\partial^2 \phi}{\partial x^2} + D_y \frac{\partial^2 \phi}{\partial y^2} - u_x \frac{\partial \phi}{\partial x} - u_y \frac{\partial \phi}{\partial y} = 0 \qquad (3)$$

In conditions when the environment is isotropic with respect to diffusion, the equation (3) states:

$$D \frac{\partial^2 \phi}{\partial x^2} + D \frac{\partial^2 \phi}{\partial y^2} - u_x \frac{\partial \phi}{\partial x} - u_y \frac{\partial \phi}{\partial y} = 0 \qquad (4)$$

Different methods can be used to solve this equation, such as finite element method, Galerkin, etc., elaborated and unstructured Euler-type schemes, Crank-Nicolson of finite differences, etc. [3] [6] [7].

Convection Diffusion Equation solution with Crank - Nicolson scheme

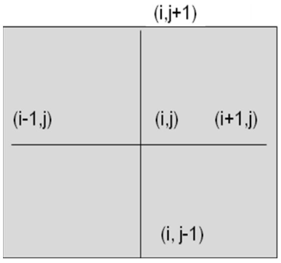


Figure 4. Five-point scheme on a two-dimensional surface

According to the finite five-point spacing scheme in the two-dimensional space (Figure 4), the equation (3) approximates in the form [18] [20]:

$$\phi_{i,j}^{n+1} = \frac{\phi_{i,j}^{n}}{2} + \Delta t \cdot \theta \left\{ \left[-u_x \frac{\phi_{i+1,j}^{n+1} - \phi_{i-1,j}^{n+1}}{2\Delta x} + \frac{\Gamma_x}{\rho} \frac{\phi_{i+1,j}^{n+1} - 2\phi_{ij}^{n+1} + \phi_{i-1,j}^{n+1}}{\Delta x^2} \right] \left[-u_y \frac{\phi_{i,j+1}^{n+1} - \phi_{i,j-1}^{n+1}}{2\Delta y} + \frac{\Gamma_y}{\rho} \frac{\phi_{i,j+1}^{n+1} - 2\phi_{ij}^{n+1} + \phi_{i,j-1}^{n+1}}{\Delta y^2} \right] \right\} + \tag{5}$$

$$\frac{\phi_{i,j}^{n}}{2} + \Delta t \cdot (1-\theta) \left\{ \left[-u_x \frac{\phi_{i+1,j}^{n} - \phi_{i-1,j}^{n}}{2\Delta x} + \frac{\Gamma_x}{\rho} \frac{\phi_{i+1,j}^{n} - 2\phi_{ij}^{n} + \phi_{i-1,j}^{n}}{\Delta x^2} \right] \left[-u_y \frac{\phi_{i,j+1}^{n} - \phi_{i,j-1}^{n}}{2\Delta y} + \frac{\Gamma_y}{\rho} \frac{\phi_{i,j+1}^{n} - 2\phi_{ij}^{n} + \phi_{i,j-1}^{n}}{\Delta y^2} \right] \right\}$$

where θ - Crank – Nicolson coefficient $0 \le \theta \le 1$

$\phi_{i,j}^{n+1}, \phi_{i,j}^{n}$ Respectively are the concentrations in point (*i, j*), respectively at the time *n Δt* and *(n+1)* Δt, where Δt – elementary interval of process.

Γ_x, Γ_y is diffusion, respectively according to direction *0X*, *0Y*;

ρ - fluid density. Assume that the environment is isotropic:

$$\Gamma_x = \Gamma_y = \Gamma \tag{6}$$

If the parameter θ = ½ then:

$$\phi_{i,j}^{n+1} = \frac{1}{2}\phi_{i,j}^{n} + \frac{\Delta t}{2} \left\{ \left[-u_x \frac{\phi_{i+1,j}^{n+1} - \phi_{i-1,j}^{n+1}}{2\Delta x} + \frac{\Gamma_x}{\rho} \frac{\phi_{i+1,j}^{n+1} - 2\phi_{ij}^{n+1} + \phi_{i-1,j}^{n+1}}{\Delta x^2} \right] \right.$$

$$\left. + \left[-u_y \frac{\phi_{i,j+1}^{n+1} - \phi_{i,j-1}^{n+1}}{2\Delta y} + \frac{\Gamma_y}{\rho} \frac{\phi_{i,j+1}^{n+1} - 2\phi_{ij}^{n+1} + \phi_{i,j-1}^{n+1}}{\Delta y^2} \right] \right\} \tag{7}$$

$$+ \frac{\phi_{i,j}^{n}}{2} + \frac{\Delta t}{2} \left\{ \left[-u_x \frac{\phi_{i+1,j}^{n} - \phi_{i-1,j}^{n}}{2\Delta x} + \frac{\Gamma_x}{\rho} \frac{\phi_{i+1,j}^{n} - 2\phi_{ij}^{n} + \phi_{i-1,j}^{n}}{\Delta x^2} \right] \left[-u_y \frac{\phi_{i,j+1}^{n} - \phi_{i,j-1}^{n}}{2\Delta y} + \frac{\Gamma_y}{\rho} \frac{\phi_{i,j+1}^{n} - 2\phi_{ij}^{n} + \phi_{i,j-1}^{n}}{\Delta y^2} \right] \right\}$$

or summarily:

$$\Phi_{i+1,j}^{n+1} \left(A_x - B_x\right) + \left(2B_x + 1\right)\Phi_{i,j}^{n+1} - \left(A_x + B_x\right)\Phi_{i-1,j}^{n-1} \tag{8}$$

$$\Phi_{i,j+1} \left(A_y - B_y\right) + \left(2B_y\right)\Phi_{i,j}^{n+1} - \left(A_y + B_y\right)\Phi_{i,jn-1}^{n+1} = \Phi_{i,j}^{n} \tag{9}$$

where

$$A_x = \frac{u_x \Delta t}{2\,\Delta x}, \qquad A_y = \frac{u_y \Delta t}{2\,\Delta y}, \qquad B_x = \frac{D_x \Delta t}{\Delta x^2}, \qquad B_y = \frac{D_y \Delta t}{\Delta y^2}, \tag{10}$$

If we note:

$$\begin{aligned} a_1 &= -\left(A_x + B_x\right) \\ a_2 &= 2\left(B_x + B_y\right) - 1 \\ a_3 &= \left(A_x - B_x\right) \\ a_4 &= -\left(A_y + B_y\right) \\ a_5 &= \left(A_y - B_y\right) \end{aligned} \tag{11}$$

Then the above equation is written:

$$a_1 \Phi_{i-1,j}^{n+1} + a_2 \Phi_{i,j}^{n+1} + a_3 \Phi_{i+1,j}^{n+1} + a_4 \Phi_{i,j-1}^{n+1} + a_5 \Phi_{i,j+1}^{n+1} = \Phi_{i,j}^{n} \tag{12}$$

Where a_i = 1, 2, 3 4, 5 are coefficients that depend on the geometric and physical properties of the system.

Below we will present some results with the aforementioned sketch of the finite difference method in an R^2 and some of its applications in the study of diffusion-convection processes in rivers and channels.

MODELING AND IMPLEMENTATION

Modeling the transport of pollutants

To assess the environmental impact of pollution, mathematical models play a major role in predicting the level of pollution in the regions considered. Below we give an implicit central space spatial schema and a forward-timing approach in time for estimating the overall transport equation [2] [6].

The description of the transport of pollutants requires the solution of the saturated water equation and the convection-dispersion-reaction equation for the transport of pollutants into the porous environment. For impregnated underwater areas, the transport of pollutants is assumed (untrue) to be an isothermal equation and the heat equation is not indispensable. The microscopic pollutant transport model equation has been developed using a small representative's element of the underwater volume [10] [11].

All these modes of transport of pollutants are solved with the diffusion-convection equation. This study takes into account different mathematical models that can be used in simulating the distribution of pollutants in aquatic environments: we also consider numerical resolution, through the central approach of finite differences, to the 2-dimensional transport model. The solution of the convection diffusion equation has been applied to the unplanned scheme in Crank-Nicolson's plan.

Dissemination of pollutants into the river, implementation of the Crank-Nicolson plan

We consider the surface of the river as a 2-dimensional, rectangular domain with coordinates (x, y), which contains the average concentration of contamination C. Thus, the steady state representation of the steady state can be given by the equation:

$$\upsilon.\nabla c = \nabla.\left(D\nabla c\right) + S \tag{13}$$

where:

S- Pollutant source,
v- the horizontal speed ,
D- diffusion coefficient.

This problem is the representative of the diffusion-convection problem if D is independent of C. In a closed isotropic plane area in which the diffusion-convection process is stable:

The model data: $\rho = 1,\ \Gamma_x = \Gamma_y = 0.1, \quad \Delta x = 0.1,\ \Delta y = 0.1, \quad \Delta t = 0.01$

Border conditions and speeds are given in the table 1:

Table 1. Boundary conditions and fluid flow velocities

Node	Φ	u_x	u_y	Node	Φ	u_x	u_y	Node	Φ	u_x	u_y	Node	Φ	u_x	u_y
1	0	1	0	6	0.2	1	1	11	0.4	2	2	16	0.6	3	0
2	0	1	0	7^x	x	1	1	12^x	x	2	2	17	0.8	3	0
3	0	1	0	8^x	x	0	1.4	13^x	x	0	2.3	18	1	0	0
4	0	1	0	9^x	x	-1	1	14^x	x	-2	2	19	0.8	-3	0
5	0	1	0	10	0.2	-1	1	15	0.4	-2	2	20	0.6	-3	0

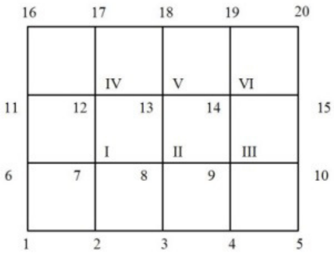
Initial conditions: $fi \Leftrightarrow \phi_i \qquad i = \overline{1,20}$

$\phi_1^0 = 0 \quad \phi_2^0 = 0 \quad \phi_3^0 = 0 \quad \phi_4^0 = 0 \quad \phi_5^0 = 0 \quad \phi_6^0 = 0.2 \quad \phi_7^0 = 0 \quad \phi_8^0 = 0 \quad \phi_9^0 = 0 \quad \phi_{10}^0 = 0.2$

$\phi_{11}^0 = 0.4 \quad \phi_{12}^0 = 0 \quad \phi_{13}^0 = 0 \quad \phi_{14}^0 = 0 \quad \phi_{15}^0 = 0 \quad \phi_{16}^0 = 0.6 \quad \phi_{17}^0 = 0.8 \quad \phi_{18}^0 = 1 \quad \phi_{19}^0 = 0.8$

$\phi_{20}^0 = 0.6$

Analytic solution



Note indices of unknowns are 7, 8, 9, 12, 13, 14 and 1,2,3,4,5,6 respectively. The latter in the figure are marked with I, II, III, IV, V, VI (Figure 5).

System of equations in nodes I, II, III, IV, V, VI is:

Node 7	$a_2^I x_1 + a_3^I x_2 + a_5^I x_4 = q_1^I - a_1^I \phi_6^0 - a_4^I \phi_2^0$	Equation I
Node 8	$a_1^{II} x_1 + a_2^{II} x_2 + a_3^{II} x_3 + a_5^{II} x_5 = q_2^{II} - a_4^{II} \phi_3^0$	Equation II
Node 9	$a_1^{III} x_2 + a_2^{III} x_3 + a_5^{III} x_6 = q_3^{III} - a_3^{III} \phi_{10}^0 - a_4^{III} \phi_4^0$	Equation III
Node 12	$a_2^{IV} x_4 + a_3^{IV} x_5 + a_4^{IV} x_{14} = q_4^{IV} - a_1^{IV} \phi_{11}^0 - a_5^{IV} \phi_{17}^0$	Equation IV
Node 13	$a_1^V x_4 + a_2^V x_5 + a_3^V x_6 + a_4^V x_2 = q_5^V - a_5^V \phi_{18}^0$	Equation V
Node 14	$a_1^{VI} x_5 + a_2^{VI} x_6 + a_4^{VI} x_3 = q_6^{VI} - a_3^{VI} \phi_{15}^0 - a_5^{VI} \phi_{19}^0$	Equation VI

Correspondence

$$\begin{array}{ll} I & \\ II & \\ III & \\ IV & \\ V & \\ VI & \end{array}\begin{cases} a_{11}x_1 + a_{12}x_2 + 0x_3 + a_{14}x_4 + 0x_5 + 0x_6 = b_1 \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + 0x_4 + a_{25}x_5 + 0x_6 = b_2 \\ 0x_1 + a_{31}x_2 + a_{32}x_3 + 0x_4 + 0x_5 + a_{16}x_6 = b_3 \\ a_{41}x_1 + 0x_2 + 0x_3 + a_{44}x_4 + a_{45}x_5 + 0x_6 = b_4 \\ 0x_1 + a_{52}x_2 + 0x_3 + a_{54}x_4 + a_{55}x_5 + a_{56}x_6 = b_5 \\ 0x_1 + 0x_2 + a_{63}x_3 + 0x_4 + a_{65}x_5 + a_{66}x_6 = b_6 \end{cases} \qquad \begin{array}{l} x_1 \Leftrightarrow x_7 \\ x_2 \Leftrightarrow x_8 \\ x_3 \Leftrightarrow x_9 \\ x_4 \Leftrightarrow x_{12} \\ x_5 \Leftrightarrow x_{13} \\ x_6 \Leftrightarrow x_{14} \end{array}$$

$$\begin{bmatrix} a_{11} & a_{12} & 0 & a_{14} & 0 & 0 \\ a_{21} & a_{22} & a_{23} & 0 & a_{25} & 0 \\ 0 & a_{31} & a_{33} & 0 & 0 & a_{36} \\ a_{41} & 0 & 0 & a_{44} & a_{45} & a_{46} \\ 0 & a_{52} & 0 & a_{54} & a_{55} & a_{56} \\ 0 & 0 & a_{63} & 0 & a_{65} & a_{66} \end{bmatrix} \begin{Bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{Bmatrix} = \begin{Bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{Bmatrix} \qquad \begin{cases} q_i = \phi_i \\ i = I, II, III, IV, V, VI \end{cases}$$

<u>Algorithm:</u>

1. Data:

- $\rho,\ \Delta x, \Delta y,\ \Delta t,\ \Gamma_x = \Gamma_y = \Gamma$ (Do not depend on the joints)
- $\phi_1^k \quad \phi_2^k \quad \phi_3^k \quad \phi_4^k \quad \phi_5^k \quad \phi_6^k \quad \phi_{10}^k \quad \phi_{11}^k \quad \phi_{15}^k \quad \phi_{16}^k \quad \phi_{17}^k \quad \phi_{18}^k \quad \phi_{19}^k \quad \phi_{20}^k$

  k = 1,2 ,3................. (initial conditions)
- $\phi_1^0 \quad ,\phi_2^0 \quad ,\phi_3^0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \phi_{20}^0$ (initial conditions)
- $u_{x1} \quad ,u_{x2} \quad ,u_{x3} \ldots\ldots\ldots\ldots\ldots\ldots u_{x20}$ (horizontal velocity)
- $u_{y1} \quad ,u_{y2} \quad ,u_{y3} \ldots\ldots\ldots\ldots\ldots\ldots u_{y20}$ (vertical velocity)

2. Size calculation for step k = 1

- $d = d_x = \dfrac{\Gamma \Delta t}{\rho \Delta x^2}$ $\qquad d = d_y = \dfrac{\Gamma \Delta t}{\rho \Delta y^2}$ (Do not depend on the borders)
- $c_x = (u_x \Delta t)/\Delta x$ $\qquad c_y = (u_y \Delta t)/\Delta y$ (për çdo pikë $\overline{1, 20}$)
- $a_1^s = -1/2\ \rho\, u_x - \dfrac{\Gamma_x}{\Delta x^2}$ $\qquad a_4^s = -1/2\ \rho\, u_y - \dfrac{\Gamma_y}{\Delta y^2}$

$$a_2^s = \frac{\rho}{\Delta t} + \left(\frac{\Gamma_x}{\Delta x^2} + \frac{\Gamma_y}{\Delta y^2} \right) \qquad a_5^s = 1/2\ \rho\, u_y - \frac{\Gamma_y}{\Delta y^2}$$

$$a_3^s = 1/2\ \rho\, u_x - \frac{\Gamma_x}{\Delta x^2} \qquad Q_i^s = \phi_i^s\ \frac{\rho}{\Delta t} \qquad s = \overline{1, 6}$$

3. Calculation of system matrix;
4. Calculation of vectors of free terms;
5. System solution;

6. Repeat the procedure for other steps k = 2,3, ... starting from point 2.

C ++ and MATLAB

The unmodified Crank-Nicolson scheme, its analytical solution, is applied for modeling the diffusion-convection equation in MATLAB and C ++ [15].

In these programs the values of the different parameters are variable.

For the model in the MATLAB the data code is presented below:

Basic starting data
Model type: 2D
Pollutants: PO_4 mg/l
Lower boundary conditions: Classic
Approximation of calculations
Total number of joints: n=56 (m=1), x = 8
Number of joints along y = 7
The coefficient that determines the time step dt = 0.1
Dynamic Domain Data:
Average speed: vx= 0.535710
vy= 0.836240
Water parameters:
The average diffusion factors: Dx= 0.55250
Dy=0.52250
Average concentration: CC=0.04318
are:
Source= 1 Point source (Point of the stationary source)
A conservative pollutant that does not undergo a change in chemical reactions

RESULTS AND DISCUSSION

Two programs were built in two different programming languages in C ++ and MATLAB. Each of them presented its advantages and disadvantages. We implemented the Crank-Nicolson numerical scheme for the transport of pollutants, while the values of the different parameters are variable (Figure 6).

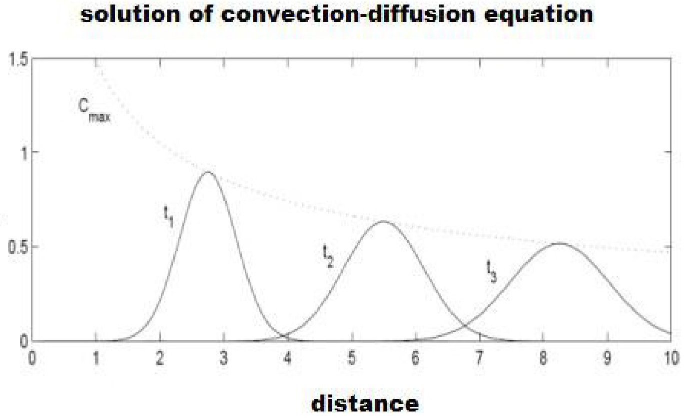


Figure 6. Illustration of C_{max} dependence on the time and distance of the pollutant source

C++

When executing the C ++ model, the program runs quickly from a computer with normal execution 1GB RAM, 80GB HDD CPU 1.7GHz, Windows 2000 environment, but for graphic presentation of the results of this C ++ solution it was not cozy. The results had to be transferred to Excel by creating an *.xls file. This file is compatible for use in the Surfer program, for the construction of the polluter distribution maps.

From these maps it is noticed that the chemical (chemical substance) diffusion diffuses into the fluid environment in function of the distance, after a certain time of day accompanied by the reduction of concentration (Figures 7, 8, 9).

In the vector map is given the direction of the chemical distribution of the chemical substance. On the most isolate map, the concentration range of the chemical substance and the distance concentration values from the pollutant source or the metering point are given. In the map with light shadow (stain) is given another way of distribution of chemical substance distribution, in the most illuminated area the concentration is greater, and distance away from the pollutant source (metering point) this illumination is decreasing Until the same uniform color is achieved.

MATLAB

While in MATLAB modeling during the implementation of the program it was noted that MATLAB is more comfortable in constructing graphical representation of the results of the convection diffusion equation solution.

The modeling results with MATLAB from the diffusion-convection equation are given below in Figure 10 and 11. From the simulation of the transport model of pollutants by applying the Crank-Nicolson numerical scheme, while the values of the different parameters are variable, we have generally reduces pollutant concentration.

For variable diffusion coefficient terms, we see that when the value of this coefficient is high, the pollutant concentration decreases faster. For variable speed of the pollutant we noticed that the concentration of high-speed contaminants is lower in value than for low flow velocity values.

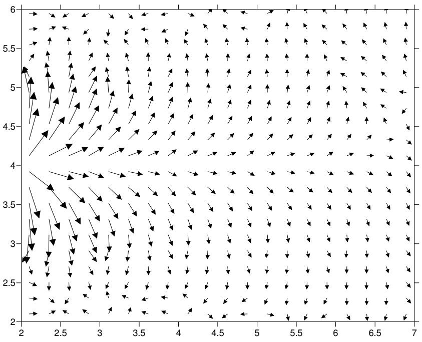


Figure 7.
Vector map of concentration distribution

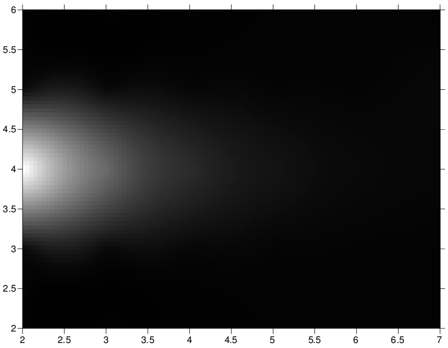


Figure 8.
Stain map of concentration distribution

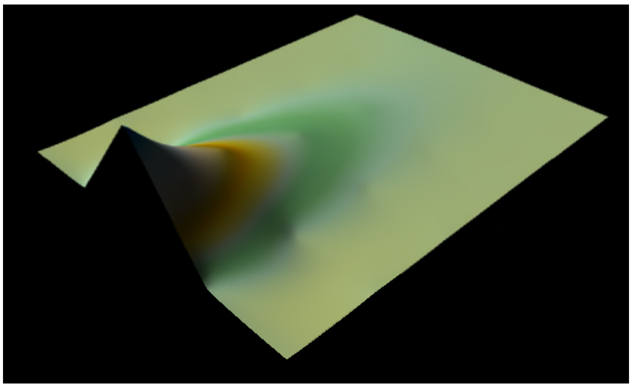


Figure 9.
3D map of concentration distribution.

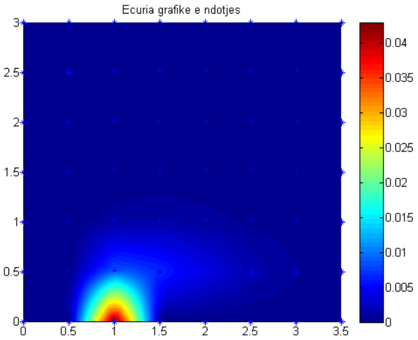


Figure 10. Distribution of pollutant concentration (MATLAB)

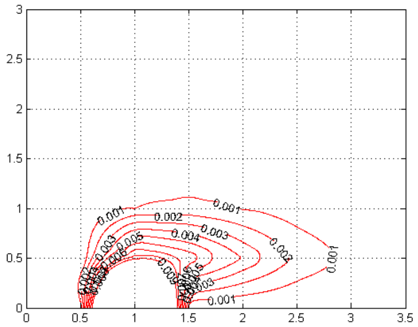


Figure 11. Concentration distribution (iso lines) (MATLAB)

REFERENCES

1. A. Kreft and A. Zuber, "*On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions*", Chem. Eng. Sci. 33, 1471-1480, 1978
2. A. Bode, S. Osmani , *"Using stochastic finite element in geostatistics and diffusion convection equation".* Proceedings, Volume I pp. 259, 3-rd International Conference on Approximation methods and numerical Modelling in Environment and natural Resources MAMERN'09, Pau, France- June 8 – 11, 2009; ISBN 978-99943-1-261-0
3. A. Cullaj, "*Kimia e Mjedisit*", Shblu, Tiranë, 2010
4. Copenhagen, Denmark: European Environment Agency. 1998
5. DeFigueiredo, D.B., Wrobel, L.C. (1990), "*A boundary element analysis of transient convection-diffusion problems*", in Brebbia, C.A., Tanaka, M., Honma, T. (Eds), Boundary Elements XII, Vol. 1, Computational Mechanics Publications, Southampton and Springer-Verlag, Berlin
6. Ding, D., Liu, P-F. (1989), *"An operator-splitting algorithm for two-dimensional convection -dispersion-reaction problems"*, International Journal for Numerical Methods in Engineering, Vol. 28, pp. 1023–40.
7. http://www.epa.gov/athens/wwqtsc/index.html, 2008.
8. J.D. Logan and V. Zlotnik, "*The convection-diffusion equation with periodic boundary conditions*", Appl. Math. Lett. 8 (3), 55-61, 1995
9. Jes Karper and Ed Boles, "*Human Impact Mapping of the Mopan and Chiquibul Rivers within Guatemala and Belize With Comments on Riparian Forest Ecology, Conservation and Restoration* ", 2004
10. Jinn-Liang Liu, "*Convection-Diffusion-Reaction Model",* Department of Applied Mathematics, National University of Kaohsiung, Elsevier Science, 2007
11. Jobson, E.H. , "*Enhancements to the Branched Lagrangian Transport Modeling System*", U.S. 1997

12. John S. Gulliver, "*The Global Perspective on Environmental Transport and Fate"*, Cambridge University Press, 978-0-521-85850-2 - Introduction to Chemical Transport in the Environment, 2009
13. Li, S-G., Ruan, F., McLaughlin, D. (1992), *"A space-time accurate method for solving solute transport problems"*, Water Resources Research, Vol. 28 No.9, pp.2297–306.
14. M.Th. van Genuchten and W.J. Alves, "*Analytical solutions of the one-dimensional convective-dispersive solute transport equation"*, U.S. Department of Agriculture, Agricultural Research Service, Technical Bulletin No. 1661, Government Printing Office, Washington, D.C. 1982
15. NRC (National Research Council), "*Restoration of Aquatic Ecosystems"*. Washington, DC: National Academy Press. 1992
16. [16] P. Howard, "*Partial Differential Equations in MATLAB 7.0"*, Spring, 2005
17. Peter Reichert, Dietrich Borchardt, Mogens Henze, Wolfgang Rauch, Peter Shanahan, László Somlyódy, Peter A. Vanrolleghem, *"IWA Task Group on River Water Quality Modelling, Scientific and Technical Report No. 12",* River Water Quality Model No. 1, © 2001 IWA Publishing
18. Petr Knobloch, "*Numerical solution of convection-diffusion equations using upwing techniques satisfying the discrete maximum principle"*, Proceedings of the Czech-Japanese Seminar in Applied Mathematics, 2005
19. Ruperto P. Bonet Chaple, "*Numerical Stabilization of Convection-Difusion-Reaction Problems"*, Delft Institute of Applied Mathematics, Web page: //www-ma1.upc.es, 2006
20. Spalding, D.B. (1972), *"A novel finite difference formulation for differential expressions involving both first and second derivatives",* International Journal for Numerical Methods in Engineering, Vol. 4 pp.551–9.
21. UNESCO 2005, "*Water Quality Modeling and Prediction",* Water Resources Systems Planning and Management – ISBN 92-3-103998-9.

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IMPROVEMENT OF THE ECONOMIC EFFECT IN COAL MINE „VRSKA CUKA" PRODUCTION OF FILTER-ANTHRACITE®

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ABSTRACT

Coal mine "Vrska Cuka" is a one of eight active mines which operates within JPPEU Resavica. With the current annualy production (5.000 to 7.000 tons) and marketing of anthracite coal as an energy source, there is a question of sustainability of this mine in the future.

With the planned production capacity of 15.000 tons of run-of-mine anthracite coal and using of new product (filter-anthracite®) for treatment of drinking waters as well as the selling prices of 750 EUR/t, there is the possibility of improving the economic effects.

Filter-anthracite® is a natural filtration material, manufactured by separation process and mechanical treatment from select grades of anthracite coal, which is produced in coal mine Vrska Cuka. In this paper is given results of the economic analysis and justification of production of the filter-anthracite® in coal mine „Vrska Cuka" Avramica.

Key words: coal mine, Vrska Cuka, filter-anthracite®, drinking water, economic analysis.

INTRODUCTION

Coal mine "Vrska Cuka" Avramica is located near Zajecar (about 10 km) in eastern Serbia. Anthracite coal is the oldest geological coal, which is mined by underground exploitation in Serbia. It represents an energy raw material with high level of carbonization. High-quality anthracite coal generates in two varieties as amorphous and crystallite [1].

Coal mine "Vrska Cuka" has been operating for more than 130 years with average annual production of between 10 and 12 thousand tons. Current production capacity is 5.000 to 7.000 tons of run-of-mine anthracite coal annually. Average ash content is about 30 % [2].

Also, coal mine "Vrska Cuka" has a modern technology for raw coal separation. The industrial plant was built 1992 and it comprises of a complex technological process for gravity and flotation concentration of raw coal. Size fractions between 0,5 and 25 mm are treated by dense-medium processes, whereas flotation has been proposed for sizes finer than 0,5 mm. A complete production is distributed on the market as an energy source in the form of raw, milled raw and/or separated anthracite.

In the present state of exploitation, production and marketing of anthracite to consumers as an energy source, there is a question of sustainability and closure of the mine in the future. The sustainability of mining production is based on [2]:

- Achieving and maintaining an annual output of 15.000 tons of commercial coal, as well as maintaining stable production over a longer period.
- The production of filter-anthracite® as well as other high quality technological products into the future.

PRODUCTION AND APPLICATION OF THE FILTER-ANTHRACITE®

Filter-anthracite® is a natural filter material, produced from crushed and sieved highest quality crystalline anthracite from coal mine Vrska Cuka, Serbia, without chemical and thermal activation process.

Filter-anthracite® is a resistant to abrasion. It is characterized by metallic-glass shine, shell texture and sharp edges, ie. rough surface with inner porous structure, which makes it suitable for filtration.

Technical characteristics of the filter anthracite® are as follows [2]:
Granulation: 0,8 - 1,6 mm and 1,4 - 2,5 mm,
Ash content: 3,5 - 5 %
The content of C-fix: 90 - 92 %
Bulk density 700 - 730 kg/m^3,
Density: 1400 - 1450 kg/m^3,
Hardness: 4 Mohs,
Volatile content: 5,5 to 10,0 %
The soluble solids content in acids: $\leq$ 0,1 %.

There are two main assortment of the filter-anthracite® with various size range: 0,8-1,6 mm and 1,4-2,5 mm. On request of the consumer, there is a possibility of production and other assortment in terms of size and ash content.

Filter-anthracite® meets the requirements of the European standard EN 12909 (in accordance with ANSI/AWWA B100-09) and in terms of the controlled parameters; it is health safety and can be used in the water purification process for drinking-water (Certificate no. 178 of 11.04.2014 by Institute of Public Health "Dr. Milan Jovanovic Batut") [2-3].

Filter-anthracite® is an effective water filtration media for single - or multi-layer filtration in the open and closed filters. It is used in the water purification for drinking-water [2-4], swimming pools water and wastewater [4-6].

A main and key activity in the future will be the construction of the industrial plant for the production of the filter-anthracite®. Technological scheme of production of the filter-anthracite® in coal mine Vrška Cuka is given on figure 1.

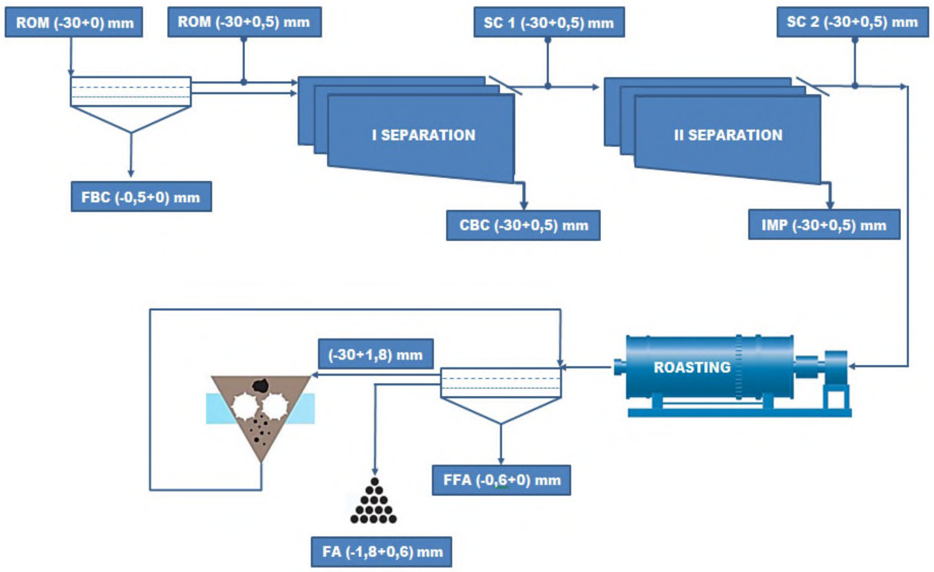

Figure 1. Technological scheme of production of the filter-anthracite®
in coal mine Vrska Cuka

Total investments amounts 100.000 EUR for the purchase of the following equipment:

1. Rotary dryer,
2. Crushing roller with a system for transporting and dosing of material,
3. Vibratory sieve with a system for dosing material,
4. The system for central dusting of technological lines,
5. The equipment for measuring and packaging the final product.

The projected annual production capacity of filter-anthracite® is 1.500 tons with product selling price of 750 EUR/t.

ECONOMIC INDICATORS

Coal mine "Vrška Cuka" sold anthracite coal as an energy source to CRH Popovac cement plant, while a smaller amount (negligible) sold as filter-anthracite® for treatment of drinking water. The main reason is that coal mine does not possess an industrial plant which high-quality separated coal with 6 % ash processing into final products, the filter-anthracite®.

The current average cost of run-of-mine anthracite coal is 7.820 RSD per ton. With the projected annualty capacity of anthracite coal of 15.000 t, total revenue will be 117.300.000 RSD or 938.400 EUR

With the planned production capacity of 15.000 tons, using of filter-anthracite® for treatment of drinking waters and other by-products, economic indicators are quite different as can be seen in Tables 1 and 2.

Table 1. Mass bilans of the filter-anthracite® production with product's selling price and its purpose of the final products

Products	Product size class	Mass share (%)	Average ash (%)	Unit price (EUR/t)	Purpose
Run-of-mine (ROM)	(-30+0) mm	100	32		
Run-of-mine (ROM)	(-30+0,5) mm	60	30		
Fine Brickyard Coal (FBC)	(-0,5+0) mm	40	35	60	Wastewater CRH Popovac
Separated Coal 1 (SC 1)	(-30+0,5) mm	40	15-17		
Coarse Brickyard Coal (CBC)	(-30+0,5) mm	20	60	60	CRH Popovac
Separated Coal 2 (SC 2)	(-30+0,5) mm	12	5-6		
InterMediate Product (IMP)	(-30+0,5) mm	28	20-25	150 100	Wastewater CRH Popovac
Filter Anthracite (FA)	(-1,8+0,6) mm	10	5-6	750	Drinking water
Fine Filter Anthracite (FFA)	(-0,6+0) mm	2	5-6	750	Granulated filter anthracite or SiC

Table 2. Total incomes with annual capacity of 15.000 tons

Products / Size class	Annual sales (t)	Unit product`s price (EUR/t)	Incomes (EUR)
FBC (-0,5+0) mm	6.000	60	360.000
CBC (-30+0,5) mm	3.000	60	180.000
IMP (-30+0,5) mm	4.200	150 / 100	630.000/420.000
FA (-1,8+0,6) mm	1.500	750	1.125.000
FFA (-0,6+0) mm	300	750	225.000
TOTAL:	15.000	/	2.520.000/2.310.000

From table 2 can be seen that using the separated intermediate in wastewater treatment, the total incomes amounts 2.520.000 EUR. If this intermediate product used in the cement industry, total incomes will amount 2.310.000 EUR. The difference between incomes is 210.000 EUR. This fact shows that the need to continue with the researching, development of technology and application of anthracite in wastewater treatment.

According to the quality and physical and chemical characteristics of anthracite, the existence of modern and contemporary plant for the separation coal, as well as the possibility of obtaining products with low ash content and high selling price, has made a concrete contribution to the improvement of the economic effects in coal mine Vrska Cuka.

CONCLUSION

Coal mine "Vrška Cuka" with production and sales of filter-anthracite® and other by-products will achieve total incomes of 2.520.000 EUR. A total cost is 2.259.000 EUR. Difference between total incomes and costs is the annually gross profit, which amount 261.000 EUR. With income tax of 10 % or 26.100 EUR, net profit is 234.900 EUR.

With a production of filter-anthracite® for treatment of drinking and wastewater, coal mine Vrska Cuka would operate economically justified, which would enable life and development of this coal mine, which is located in the border and underdeveloped area of Eastern Serbia.

REFERENCES

- Stakic, B. et al., (2006) Study on reserves of coal deposits „Mala Čuka" Avramica.
- Sokolović, J., Stakić, B., Perendić, S., (2017) Sustainable use of resources in the coal mine Vrska Cuka: Application of anthracite coal for water treatment, Plenary lectures, Proceedings of VIII Symposium with international participation "Mining 2017", 16 - 18 May 2017., Palic, Serbia, pp. 72-84.
- Perendic, S., Ciric, D., Stakic, B., Sokolovic, J., (2015) Application of the filter-anthracite® for drinking water purification", Proceedings of XXIII International Scientific and Professional Meeting „Ecological Truth", Eco-Ist '15, 17 - 20 June 2015, Kopaonik, Serbia, pp. 610-613.
- Ciric, D., Stakic, B., Perendic, S., (2014) Usage of anthracite in drinking and wastewater purification, Proceedings of XXII International Scientific and Professional Meeting „Ecological Truth", Eco-Ist '14, 10 - 13 June 2014, Bor Lake, Bor, Serbia, pp. 414-419.
- Sokolovic, J., Stanojlovic, R., Stankovic, S., Gardic, V., (2014) Treatment of oily wastewater by adsorption using anthtracite, Quaestus Multidisciplinary Research Journal, Quaestus No. 4 / February 2014 (2014), pp. 290-297.
- Stakic, B., Sokolovic, J., Perendic, S., Ciric, D., (2015) Purification of industrial oily wastewater by anthracite from coal mine „Vrska Cuka" Avramica", Proceedings of X International Symposium on Recycling Technologies and Sustainable Development – X IRTSD 2015, November 04-07, 2015, Bor, Serbia, pp. 109-112.

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WATER QUALITY MODELING IN LAKES

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ABSTRACT

Mathematical modeling is often used in the field of environmental protection.In this manuscript is presented analysis of the polluting substances content discharged in lake. This type of mathematical model is based on the use of the ordinary differential equations. This paper gives an example of lake pollution modeling. Here is shown a general model of polluting substances concentration in lake and wide range of possible cases that can be applied in model.

Key words: lakes, modeling, water quality, ordinary differential equation.

INTRODUCTION

Mathematical modeling is based on theoretical approach. Fundamental theories and principles governing the system along with simplifying assumptions are used to derive mathematical relationships between the significant variables. The resulting model can be calibrated using historical data from the real system and can be validated using additional data. Predictions can be made with predefined confidence.

Mathematical modeling involves the transformation of the system under study from its natural environment to a mathematical environment in terms of abstract symbols and equations. The symbols have well-defined meanings and can be manipulated following a rigid set of rules or “mathematical calculi.” Theoretical concepts and process fundamentals are used to derive the equations that establish relationships between the system variables. By feeding known system variables as inputs, these equations or “models” can then be solved to determine a desired, unknown result.

Mathematical modeling is widely used in the field of environmental protection.There is a very advantageous application of the mathematical modeling in analyzing of polluting substances fate and transport in different environments such as water, air and soil. In this manuscript will be presented analysis of the polluting substances content that are discharged in surface water (lake). This type of mathematical model is based on the use of differential equations of the first order.

MATHEMATICAL METHOD

In analysis of the fate of a substance discharged into a lake, the lake can be characterized as a completely mixed system. This assumption may be justified for shallow lakes. Larger lakes may be compartmentalized, and each compartment may be analyzed as completely mixed, with interactions between compartments. It is therefore useful to begin the modeling of lakes assuming completely mixed conditions. In that case, because the concentration of the substance in the outlet of the lake is the same as that inside the lake, the general form of the mass balance equation is as follows:

$$\frac{d(V_t C_t)}{dt} = Q_{in,t} C_{in,t} - Q_{out,t} C_t \pm r V_t \tag{1}$$

Where:

- Vt is the time-dependent volume of the lake (m^3),
- Ct is the time dependent concentration of the substance in the lake (kg/m^3),
- Qin,t is the time-dependent volumetric flow rate into the lake (m^3/s),
- Cin,t is the time dependent concentration of the substance in the influent (kg/m^3),
- Qout,t is the time-dependent volumetric flow rate out of the lake (m^3/s),
- r is the time independent reaction rate of the substance in the lake (kg m^3/s), and
- t is the time (s).

As a first step in modeling a lake and simulating its response to various perturbations, the above general equation may be simplified by invoking the following assumptions: the lake volume remains constant at V, the flow rate into and out of the lake are equal and remain constant at Q, the concentration of the substance in the influent remains constant at C_0, and all the reactions inside the lake are consumptive and of first order, of rate constant, k (s^{-1}). With the above assumptions, using C instead of Ct :

$$V\frac{dC}{dt} = QC_{in} - QC - kVC \tag{2}$$

$$\frac{dC}{dt} = \frac{QC_{in}}{V} - \frac{(QC + kVC)}{V} = \frac{QC_{in}}{V} - \left(\frac{Q}{V} + k\right) C \tag{3}$$

$$\frac{dC}{dt} + \left(\frac{Q}{V} + k\right) C = \frac{QC_{in}}{V} \tag{4}$$

$$\frac{dC}{dt} + \alpha C = \frac{W}{V} \tag{5}$$

$$\alpha = \left(\frac{Q}{V} + k\right) = \left(\frac{1}{\tau} + k\right) \tag{6}$$

Where:

- $\tau = \frac{V}{Q}$ is hydraulic resistence time of lake (s), and
- $W = QC_{in}$ is the load flowing into the lake (kg/s).

The simplifying assumptions make it easier to analyze the response of a lake under various loading conditions. Results from such simple analyses help in gaining a better understanding of the dynamics of the system and its sensitivity to the system parameters. With that understanding, further refinements can be incorporated into the simple model, if necessary.

One of the elementary scenarios that can be simulated is the steady state condition to determine the in-lake concentration, *C*ss , of a substance caused by a continuous, constant input load of *W*. The steady state condition is found by setting the first term in the left-hand side of Equation (5) to zero, yielding:

$$C_{ss} = \frac{W}{V\alpha} = \frac{W}{V\left(\frac{1}{\tau}+k\right)} = \frac{QC_{in}}{V\left(\frac{1}{\tau}+k\right)} = \frac{C_{in}}{(1+k\tau)} \qquad (7)$$

A more general situation, where the application of a new step load to a lake with an initial concentration of *Ci* causes a transient response, can be simulated by Equation (5), giving the solution as follows (Schnoor, 1996):

$$C = C_0 exp\left[-\left(\frac{1}{\tau}+k\right)t\right] + \frac{C_{in}}{1+k\tau}\left\{1 - exp\left[-\left(\frac{1}{\tau}+k\right)t\right]\right\} \qquad (8)$$

It is apparent that, by setting *t* to infinity, the first term in the right-hand side of Equation (8) dies off to zero, and the second term approaches the steady state value given by Equation (7). The above equations can be applied to model the fate and transport of several water quality parameters such as pathogens, BOD, dissolved oxygen, nutrients, organic chemicals, metals, etc. Once the water column concentrations of these are established from the above equations, their impacts on other natural compartments of the lake systems such as suspended solids, biota, fish, sediments, etc., can also be analyzed. The above results can also be applied to simulate lakes in series and compartmentalized lakes.

RESULTS AND DISCUSSION

Consider a lake, of certain volume, V, with a flow rate of Q leaving the lake. The lake receives a waste load, W(t), where it is consumed by first-order reactions. The objective is to develop a model to relate the resulting concentration, C, of the pollutant in the lake to the system variables under a range of loading and initial conditions. This problem can be modeled based on an material balance on the pollutant in the lake. Assuming the lake to be completely mixed and to be of constant volume, this statement can be expressed in the form of the differential equation (2).

$$\frac{dC}{dt} = \left(\frac{W_{(t)}}{V}\right) - \left(K + \frac{Q}{V}\right)C \qquad (9)$$

where K is the sum of the first-order rate constants for all the consumptive reactions. The solution to the above ordinary differential equation can yield the concentration of the pollutant in the lake, C, as a function of time under predefined initial conditions, C_0, and forcing waste load functions, W(t). The forcing functions can be some function of time, continuous or discontinuous. Obviously, the nature of W(t) should be known before attempting to solve this ordinary differential equation. A general solution to the above can be found from the following:

$$C = \frac{e^{-\alpha t}}{V} \int W_{(t)} e^{\alpha t} dt + C_0 e^{-\alpha t} \tag{10}$$

where α is as in (6).

Obviously, the result will depend on the nature of the forcing function, W(t). The simplest case is the steady state solution, as in (7):

$$C_{ss} = \frac{W_0}{V \cdot K + Q} \tag{11}$$

where Css is the concentration of the pollutant in the lake at steady state. Because the explicit solution for the problem as described by the general equation (9) will depend on the initial conditions and the forcing function, it is desirable to develop simulation models that can solve the governing equations in a general manner rather than in a problem-specific manner. Some common types of W(t) functions in this problem are as follows:

- constant loading: $W(t) = W_0$
- linearly increasing or decreasing load: $W(t) = W_0 \pm at$
- exponentially increasing or decreasing load: $W(t) = W_0\, e^{\pm\lambda t}$
- step increase or decrease from a background load of W_0: $W(t) = W_0$ for $t < 0$ and $W(t) = W_0 \pm W$ for $t < 0$
- impulse load of mass, m: $W(t) = m\delta(t)$, where $\delta(t) = 0$ for $t \neq 0$ and $\int(-\infty, \infty)\, \delta(t)dt = 1$
- sinusoidal loading: $W(t) = W_{ave} + W_0 \sin(\omega t - \theta)$

By combining the above simple functions, several different real-life loading scenarios can be approximated for modeling purposes. Many of these functions are amenable for analytical solutions, while all of them can be analyzed numerically. However, if parameters of this model are also time-dependent, such as the flow rate, Q, for example, then the solution has to be found through numerical simulation. As such, it is desirable to select software packages that can be readily adapted for numerical analysis. Those that have built-in routines for numerical analysis will be preferable for building realistic models.

CONCLUSION

Mathematical modeling, applied in environmental protection, gives opportunity to environmental analysts for fast, efficient and cost-effective assessment of the situation, with the possibility of short-term and long-term effects on the environment consideration. General models, with slight modifications, can have a wide range of application for a variety environments and conditions under consideration. This paper is an example of lake pollution modeling because of polluting substances discharging. It is shown a general model of polluting substances concentration in lake and wide range of possible initial conditions that can easily be applied in model.

REFERENCES

1. Chapra, S. C. (1997) Surface Water-Quality Modeling, McGraw-Hill, New York.
2. James, A. (1993) An Introduction to Water Quality Modeling, John Wiley & Sons, New York.
3. Schnoor, J. L. and O'Connor, D. J. A steady state eutrophication model for lakes, Water Res., 14, 1651–1655, 1980.
4. Thomann, R. V. and Mueller, J. A. (1987) Principles of Surface Water Quality Modeling and Control, Harper Collins Publishers, New York.

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THE ROLE OF SCIENCE AND SCIENTIFIC RESEARCH AND DEVELOPMENT OF WATER MANAGEMENT PROFESSION IN SERBIA

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ABSTRACT

Science in water management is a product of the mind to the field of water management which systematize the knowledge acquired using the methods of scientific research organizations, universities and institutes. The system formation water, circulating water, change water management systems, natural factors and human activities are the basis for the field of science in water management which to interpret phenomena, events and ways of solving problems. According to the fields of scientific study of water management belongs to the field of engineering, and the research is connected with other scientific fields, and the natural, social, medical, humanitarian and philosophical, biotechnology and information sciences.

Key words: science, scientific research, development , water management.

INTRODUCTION

Methods of investigation in water management as the primary experimental with the application of general and specific methodologies. The research in water management is the systematic collection of data, analysis and interpretation of information about how to resolve the problem for the events around the water in a way that meets the needs of users.

Scientific research water management Serbia comprises the steps of a gradual transition from fundamental research through the development of research to enlarge the knowledge of the void and the legality of the process around the water to applied research in the implementation and practical application of solutions for the water utility and water management.

Science-and scientific research which are of particular interest in the function of the water management Serbia; hydrology, ecology, economics, agriculture, sociology, law, science of management and other scientific disciplines.

Hydrology is science the void, and its physical properties and formation circulation in nature. Hydrological research to better understand the concerns of water and the environment with feedback influence. The waterpower Serbia used research the results contained in the explanation of the cycle in the hydrological measurements, predictions, statistics. Hydro technical solutions in water management in Serbia in order to find solutions:

- reduction and predicting floods, landslides and drought,
- casualty and drinking water,
- determination networks and irrigation systems,
- define the types of facilities for the provision of water supply and hydroelectric energy production,
- foresight geomorphological changes such as the effects of erosion and deposition of sediments,
- determination of the impact of economic and anthropogenic environmental changes on water resources,
- determination of the type and intensity of the risks of pollution and
- define the routes (roads) for transporting water.

Ecology provides a scientific explanation that when using water causing damage to nature and the environment. The specific objective of environmental protection is to prevent waste. Ecology present in the field of water is, in scientific research environmental abiotic factors which are (representing the physical and chemical environmental conditions) and biotic (influences that an organism is suffering from other living beings). Research work in ecology water related to the establishment, preservation and ensuring a 'good' water status.

The role of economics in water management is neglected or is no special theory. Under the influence of changes in ownership and control areas in the world and the development of environmental economics and economics of the public sector, economics of water management are gaining importance.

It should implementation requires defining the basic elements of value in the economy of water management. Establishing the economics of water management is based on the segments of water management system that applies to the disposal (use) water, water management services and other activities, and they are turning to water as a public good, services as well as private goods and types of combinations of public private goods for common and collective use of water. Water management is scientific research activities in the field of economy needed because it will determine the theoretical rules of conduct and economic laws. Economics of water management is necessary to study in the field of water, water protection, use (exploitation) of water, especially the effects of water and water management of the environment, with the aim of developing the theory of economic assessments for decision-making on water in its "production" economic appropriation , possession and use.

Agricultural sciences are intensively offline in solving the problem of phenomena and events about water and water management in the areas of soil science of geology, agrochemicals, plant protection, irrigation, drainage, soil conservation, water use in crop production, horticulture and viticulture, and in particular in the agricultural economy.

Sociological science in water management are based on research in the social demographics, the theory of social structures and systems, sociology of work, settlements, economic sociology and others.

Legal Science in water management is involved in the development of general administrative law, administrative management, ownership and property rights, the development of the political system, financial law, labor law and others.

Contemporary (strategic) management as a separate discipline can accelerate the development of water resources through the multidisciplinary operation in research on water management and water management systems. A special contribution of management in the application of modern managerial functions of planning, organization, management, control, analysis and information in the water sector of Serbia. This discipline is necessary to study how water management, water management processes and systems with the problems that arise in the exercise of the targeted results. For management is particularly important to establish a system of leadership as a process of accurately and precisely certain tasks employees. Water management in the systematic and organized effort for the implementation of numerous scientific and practical results between which there is a link to areas and activities around water. Scientific management is contained in a quantitative and systems theory, theory-based entrepreneurship, marketing, etc.

Other scientific disciplines are those for the case studies have water technology, mechanical engineering, electrical engineering, physics, chemistry, biology and health and sanitary protection.

APPLICATION OF SCIENCE AND SCIENTIFIC RESEARCH SERBIAN IN WATER MANAGEMENT

The direction of scientific and scientific-research work in the water sector Serbia is determined by water management problems that require new knowledge on water management areas and its development. Contents of scientific research related to:

- ambition for research related to technical, economic and legal characteristics of the water problems with the use of scientific methods,
- identify areas and branches of research,
- empirical and theoretical solving problems and creating conditions for the implementation of solutions,
- application domestic and foreign achievements in the field of water management and branches,
- science-research approach to determine the hypothesis,
- develop hypotheses and research needs to be done about the situation, elements and events around the water system and for a specific time and space,
- determination of criteria feasibility research, theoretical value and practical significance,
- value determination problems and solutions through the verifiability of success.

Scientific research, he had an exceptional character and coordinated with the development of water management in Serbia. Are developed and acquired new knowledge, applied new technological processes, technology was developed in the design, construction and operation of water facilities and systems. In particular, the results of applied scientific research in agriculture, construction, transport, energy and others. Events in the past, without a strategy for the development of scientific research in the water sector have led to a loss of continuity in relation to the European and world scientific achievements [1]

Examples of well-applied scientific research papers are guaranteed determining environmental rate [2] and the planning of water management systems [3].

Research that contributes to the development of water management in Serbia refer to the science of engagement required for the implementation of the ODV, and VOS or to [4]:

- management river basin,
- integrally and integrated management of water resources,
- protection of water (of surface and ground),
- use water in water supply,
- arrangement watercourses and protection against harmful effects of water,
- use hydropower,
- hydraulic engineering land reclamation,
- application modern technology
- advancement methods and technology research, design, built, maintenance and operation of facilities and systems,
- define the economic fundamentals, instruments and measures in the areas of water management in the state and economic structure,
- influential factors for water management surroundings and environment,
- develop legislature was and normative activities,
- systematizing technical, legal and economic elements and factors in interstate and international relations in water management and water management systems.

WATER MANAGEMENT BRANCHES

Water menagement profession in the professional skills of the term education and skills to practical work achieved a positive result. In water management it has a huge range of complexity of the simplest tasks, such as performing. Hydro workers to the most complex such as the management of flood defenses. In the history of the water management profession demonstrated a high level of knowledge and skills for the stable operation of the system, a specially in situations of problems in floods, droughts, pollution or when water is lacking. In the last decades has weakened the waist which has become a special problem of water management. In the water management profession created the experience of solving problems and is passed from generation to generations of. fluctuations and the departure of employees, not the transfer of knowledge and skills, and new employees are not passed through the theoretical and practical training. From the past to learn about the operation of the factors that negatively affect the changes in water and functioning facilities.

Water management professions in values directed to the expectation that the holders, in addition to material satisfaction, develop independence (autonomy) that is integrated into the system. Different professions create the basis for determining the causes of traffic and the status of water and proposes services to obtain benefits. Results are measured in technical and economic impacts, particularly impacts on the population and industries of the economy. Waist in water management is addressed in the environment where it is structural, social, economic and technological changes force the innovation of knowledge and skills. In particular, must accept the views from the environment, which constantly monitors the results of the water management profession and indicates good or bad actions taken.

Water management profession makes a collection of different professions who seek to build consistent internal relations. Profession in the system that attempt to build a harmonious interior relations. In the system of water management (water resources) theses respecting each other's values and integration.

Integrating some pike is to strengthen the position and interests of water management which is achieved by a close appreciation of knowledge, skills and the way they execute in joint activities. It is especially necessary rapprochement of certain professions water management profession because the interests of certain professions and individual goals are converted into a common goal in a particular workplace behavior functional organization. Organized by the water management must limit activities of representatives of certain professions that seem disintegration, with the introduction of proportionality in remuneration according to the intensity of the impact of certain professions in achieving the objectives. It is also important to develop information and communication between the waist of certain essential events for the creation and improvement of working conditions. In future profession in operation management should find an adequate alternative solution to the problem in a situation where classically method that can not be achieved. For the profession it is necessary to use modern technical and technological resources, new knowledge and skills in the action operation.

CONCLUSION

The role of science and scientific research in the water sector Serbia has so far yielded excellent results, and the application have been removed causes harmful effects of water and water pollution. Necessarily approach changes, events, influences and pressures on water within the educational and research institutions which have contributed to the development of water management profession. She has developed practical work in situations that require quick response (floods, disasters), a lessons learned employees are interactive posed new tasks for arriving at scientific and research to improve the profession have a common influence on the efficiency of water management, which requires a multidisciplinary and development; human resourced.

REFERENCES

1. Bajčetić, M. Marko: Value system of water management 2010.
2. Djordjevic, B, Dasic T.: The determination of the guaranteed ecological flows water management, Belgrade page 26-34 (2000)
3. .Djordjevic, B. Depending bit key ecological planning water management systems page 175-176; 5-6 (1998)
4. Ministry of Agriculture, Forestry and Water Management: Water Management Plan Republic of Serbia Institute Jaroslav Cerni, Belgrade , page 366-369 .

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CHARACTERISTICS OF WATER SUPPLY SYSTEM IN NIS AND QUALITY LEVEL OF DRINKING WATER

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ABSTRACT

Water supply system of Niš has no major problems and it is in a very good condition both in the amounts of water resources and in the quality of its water. This situation is mainly due to favorable geographical position, availability of clear water springs and the fact that all of them function in such a way so that demands for water in this region are always satisfied. Quality level of drinking water is high and it should be maintained in the same way through constant surveillance and improvement.

Key words: water supply, water sources, water quality.

INTRODUCTION

With two thirds of the Earth’s surface covered by water and the human body consisting of 75 percent of it, it is evident that water is the crucial part of our planet and life on it. Moreover, water is an integral part of the Earth's biogeochemical process that creates and sustains our environment. Consequently, water is an essential resource for many human activities required to sustain our current society and it plays a major role in regional development.

Increasing population in the world as well as industry and agriculture development and their intensity can put a strain on water supply and maintenance of its quality. According to the World Health Organization 91% of the world’s population had access to an improved drinking water sources in 2015, compared with 76% in 1990. On the other hand, contaminated drinking water is estimated to cause 502 000 diarrhoeal deaths each year. It is estimated that by 2025, half of the world’s population will be living in water-stressed areas.

The safety and accessibility of drinking water are major concerns throughout the world. Safe and readily available water is one of the basic human rights and it is important for public health, whether it is used for drinking, domestic use, food production or recreational purposes. Drinking water must have certain characteristics and, most importantly, must not be harmful to human health. This includes chemical and microbiological quality of water and hygienic properties of water. Improved water supply and sanitation, and better management of water resources, can boost countries' economic growth and can contribute greatly to poverty reduction.

Water supply of Niš - Niš is now supplied with water through two independent water supply systems NIVOS and MOVOS. Water supply system NIVOS consists of Mediana, Studena and Ljuberadja-Niš with water springs, corresponding distribution network, pumping stations and reservoirs. MOVOS or Morava water supply system gets its water from the well Miljkovac and distributes water to villages Miljkovac, Paljina and Berčinac. They supply around 240 000 people and industry of Niš, with the amount of 37 732 608 m^3 per year or 103 377 m^3 per day.

CHARACTERISTICS OF NIVOS WATER SUPPLY SYSTEM AND QUALITY OF DRINKING WATER

The concept of NIVOS water supply system is based on the exploitation of three water supply sources. Its basic purpose to supply the citizens with clean drinking water which depends on the development of needs for water in the future, imbalance in consumption during the year, as well as of hydrological conditions in sources' basins during the year. Three water supply systems that provide drinking water to the city of Niš are as follows:

- Mediana – a source of groundwater additionally enhanced with previously purified water from Nišava river with the capacity of 100 to 500 l/s
- Ljuberadja-Niš – a number of natural springs in the karst topography such as Mokra, Krupac, Ljuberadja and Divljana, with the capacity of 800 to 1450 l/s
- Studena – natural spring in the karst topography with the capacity of 220 to 340 l/s.

Examining the available records and conducting interviews with the staff of JKP "Naissus" laboratory for the purposes of this research revealed that situation of water supply of Niš is quite favorable. Water from the spring "Studena" is used as the amount that meets the needs of consumers. Then water from springs "Mokra" and "Divljana" of the system "Ljuberađa - Niš" is put into use, and in the case of emerging needs water from springs "Krupac" and "Ljuberađa". In the whole water supply network "Mediana" acts as a backup source to cover seasonal imbalances in the amounts of other sources. The system of "Median" is turned on continuously for three to five months during the year. Above all, even when in the periods of heavy rains water in these springs becomes turbid it never happens in all springs at the same time so it is possible to put out of use turbid springs and put clear springs in use until turbid water clears out.

Characteristics of Mediana water supply system and quality of drinking water

Mediana source of groundwater is located east of Niš where natural conditions which dominate in this area imposed a solution of artificial enhancement of the aquifer. It consists of a large number of infiltration units where infiltration basin with wells is placed around the reservoir. In order to ensure optimal and long-term uninterrupted exploitation of systems for artificial recharge of aquifers a system for pre-treatment of river water has been designed and built. Pre-treatment involves deposition of suspended sediment using coagulants and water passing through some kind of slow filter.

Nišava river on the stretch of water intake is in the class IIa and it is a type of water which with the normal methods of treatment such as coagulation, filtration, and disinfection can be used for the supply of drinking water. Based on the analysis of the quality of the water in river Nišava at the measuring location of "Naissus" water supply the quality corresponds to class II, with the exception of phenol, which at times of lower water levels can appear in higher concentration than permitted.

Characteristics of Ljuberadja-Niš water supply and quality of drinking water

Water supply system Ljuberadja- Niš consists of four different water sources: Krupac, Mokra, Divljana and Ljuberadja and all of them will be analyzed separately.

Krupac well springs out from the rock mass in the village Krupac in the northwest of Bela Palanka basin. Water comes from the well at the altitude of 263 m in one submerged sinkhole. Krupac well is one of the most abundant springs of karst topography in eastern Serbia and it is the type of karst spring that seemingly dry up or reduce amount of water. These types of wells, as a rule, have deeply laid and very spacious cave channels that can accumulate large amounts of water. The amount of water in Krupac depends on climate conditions in the collecting area. Precipitation level is on average 850 mm per year, where the greatest amount of rainfall is recorder in May, and then in October or November and the least amount is recorded in September, and then in January or February. The entire amount of rainfall is absorbed through cracks in the interior of the karst, except for the part that evaporates. The average amount of water in Krupac well is 0,941 m3 / s. A month with the highest amount of water is April, and the driest October. Water quality is very high and belongs to class "I" that only with disinfection measures can be used in water supply system. According to the chemical analysis of samples water quality fully meets the requirements of drinking water. The only treatment of water that is applied is chlorination.

Mokra well is located near the village Mokra and at the foot of the Suva planina, on its eastern slopes. The water temperature of the well shows significant fluctuations in the temperature range of 11.5 to 20 °C. There is a correlation between abundance of water and the temperature. In the period of increased and maximum abundance, the temperature of the water rises up to 20 ºC. The research has been conducted and revealed that this well is a result of two different springs, whose water temperatures are different for 9 to 10 ºC. Turbid water in the well is very rare and short-lived occurrence. There is no other treatment of water except disinfection. Maximum amount of water exploited from this well is 800 l/s.

Divljana well springs from limestone massif of Suva planina on the left bank of Koritnička river, near the road Bela Palanka - Babušnica. Chemistry and the temperature of the water in this well is stable the whole year and water flow is uniform. Water temperature is constantly 12 to 13 ºC and maximum amount of water exploited is 800 l/s.

Ljuberadja well consists of series of 11 springs at a distance of a few kilometers in the valley of river Lužnica. Maximum amount of water exploited from this well for is 450 l/s.

Characteristics of Studena water supply system and quality of drinking water

Water source "Golemo vrelo" is located at the altitude of 400 meters, above the village Donja Studena on the northwest slopes of Mosor (985 m), 17 km away from Niš. It consists of 14 separate springs in total. The total amount of water of all sources can vary in certain seasons of the year from 240 l/s to more than 400 l/s. The average annual amount of water is 327 l / s. Period of reduced amount is very long, and the oscillation of the curve very slight, indicating a good, retention power of limestone mass through which the water moves. Chlorination station is part of the collecting chamber where chlorination of water is carried out. Mixing the chlorine with water takes up to 10 minutes, which allows customers to use water at the very beginning of the distribution. The water system "Studena" supplies drinking water to the villages of Donja Studena, Čukljenik, Jelašnica, Suvi Do, then Niška Banja, the city of Niš and some industrial facilities.

Control of water quality

Sanitary control of the water supply system is performed by the Sanitary Control Laboratory within the JKP "Naissus" Niš as well as in the authorized health institution, in this case Public Health Institute in Niš. In order to verify quality of its work Laboratory of JKP "Naissus" has based its work on international standard SRPS ISO/IEC 17025:2006 which means that laboratory is competent to carry out tests or calibrations, including sampling, physicochemical analysis and microbiological analysis. Besides this, even monitoring of surface waters in the river basins near the springs is conducted periodically.

Daily sample is taken from all springs, reservoirs and specified number of points in the water supply network. Physicochemical analysis and microbiological analysis of water are carried out according to the prescribed schedule and the prescribed methods**.** Water is analyzed every day of the year and daily approximately 45 samples are collected. Water quality is measured on basis of Regulations for safe drinking water (Pravilnik o higijenskoj ispravnosti vode za piće, Sl. List SRJ, br. 42/98, 44/49) and that on analysis A once a day and on analysis B once a month.

Latest available data gathered by interviewing staff of Laboratory of JKP "Naissus" is represented in Table 1. from which it can be seen that in last six months, from October 2016 until March 2017, percentage of safe drinking water is on average 98.37 % and percentage of physicochemical and microbiological parameters is very low. Considering the fact that according to the World Health Organization recommendations 20 % in physicochemical parameters and 5 % in microbiological parameters are allowed it can be concluded that situation of water quality in Niš is quite satisfying.

Table 1. Percentage of safe drinking water, physicochemical and microbiological parameters in water supply system of Niš for the period from October 2016 until March 2017

Months	Safe drinking water %	Unsafe according to physicochemical parameters %	Unsafe according to microbiological parameters %
March 2017	98.67 %	0.00 %	1.33 %
February 2017	96.98 %	2.44 %	0.6 %
January 2017	99.60 %	0.00 %	0.40 %
December 2016	99.14 %	0.00 %	0.86 %
November 2016	97.28 %	0.12 %	2.59 %
October 2016	98.29 %	0.00 %	1.71 %

The low percentage of bacteriological contamination of the water from the supply network has its undoubted confirmation in a quiet epidemiological situation in Niš. However springs in karst topography, especially in the time of turbid water, and chlorination, as the sole treatment technology, requires constant vigilance and a high degree of responsibility in the production of water. Mediana source, whose groundwater is threatened by industrial waste waters and where technologically prepared water of the river Nišava is added, demands for exploitation under the prescribed regime with rigorous sanitary control. Bacteriological and chemical inadequacy of water have been reported sporadically in the water supply network. Thanks to the organization of work of the authorized laboratory inadequacy of water was diagnosed in time, and the measures in the production of water immediate, which is why there was no threat to the health of citizens.

CONCLUSION

All mentioned water sources along with well organized distribution and monitoring system provide safe drinking water of high quality to the citizens of Niš. Due to favorable geographical position current situation of water supply system in Niš is in relatively good condition but constant surveillance, improvement and implementation of new methods in necessary and crucial in order to maintain present water quality. Possibility of contamination is unfortunately present because there are no laws that would prevent that or on the other hand laws that do exist are not being enforced on actions that could endanger lives of this and next generations.

There is a possibility of implementing new sources in water supply system through wells Pešter and Toplik but for now they are still not in function since present sources satisfy demands for water. But with the increase of the capacity of industrial facilities and population growth there is continuous trend of increasing need for drinking water. That is the reason why water supply system in Niš should be well protected, modernized, reconstructed, as well as efficiently, cost-effectively and professionally used, but also upgraded and expanded with new water supply facilities.

REFERENCES

1. UNICEF and WHO *Progress on Sanitation and Drinking Water: 2015 Update and MDG Assessment*, UNICEF, 2015
2. Ignjatović, Z., Zlatković, T., Stamenković, Z. *Javno komunalno preduzeće za vodovod i kanalizaciju – Naissus stvarno dobra voda,* 39-58, Grafika Galeb, Niš, 2007
3. Radenković, Z. *Dokumentacioni elaborat o funkcionalnom stanju i izvedenim objektima na infiltracionom izvorištu Mediana,* JKP Naissus*,* Niš, 2000
4. Zakon o vodama (Službeni glasnik RS, br. 30/2010, 93/2012, 101/2016)
5. Pravilnik o higijenskoj ispravnosti vode za piće, Sl. List SRJ, br. 42/98, 44/49

A PRELIMINARY ASSESSMENT OF WATER QUALITY OF SOME SMALLER WATERCOURSES FROM SREM (VOJVODINA, SERBIA) BASED ON AQUATIC MACROINVERTEBRATES

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ABSTRACT

The investigation of small watercourses in the province of Srem was performed in November of 2015 on six localities situated at three streams. Based on recorded macroinvertebrates communities herein we provide a water quality assessment based on following metrics: total number of taxa, saprobic index, BMWP, ASPT, diversity index and percentage participation of Oligochaeta in the total macroinvertebrate community. A very low water quality was assessed downstream larger settlements (Inđija and Ruma). Our results could indicate that industrial and urban wastewaters probably act as the main treats to investigated watercourses. As only the one season (autumn) was covered in this investigation, a prolonged research is needed for more reliable data.

Key words: ecological status, saprobic indices, biotic indices, small watercourses, Pannonian Plain.

INTRODUCTION

The Pannonian Plain is a central part of the Danube basin. In Serbia it covers northern part of the country (Vojvodina). Some of the largest European rivers, such as the Danube, Sava, and Tisa Rivers flow throughout this region, alongside with number of smaller, mostly, man-made watercourses (canals) such as the Danube-Tisa-Danube (DTD) canal-network.

The south-eastern part of Vojvodina, bordered by the Danube (on the North and the East) and the Sava River (on the South), is called Srem. From the southern slopes of the Pannonian island mountain – the Fruška Gora, a numerous small watercourses (streams) arise and flow, making a unique hydrological network [1, 2].

Being one of more densely populated regions in Serbia and with large areas of agricultural lands it is not surprising that watercourses in this region are under heavy anthropogenic influences. As the main treats to these smaller aquatic habitats agricultural runoff, irrigation and canalisation, communal and industrial waste waters, could be singled out [1].

Watercourses in this region are rarely investigated, particularly considering their macroinvertebrates components and ecological status/water quality. Routine ecological monitoring is conducted only in the southern part of Srem (belonging to Belgrade region) [3].

European legislative had been set standards regarding quality of surface waters [4] and based on these recommendations in Serbia has been developed and applied a national legislative [5].

Aim of this work is to contribute to knowledge regarding usability of aquatic macroinvertebrates for water quality assessment in small watercourses of central Srem.

MATERIAL AND METHODS

The benthic samples were taken in November of 2015 at three small watercourses in Srem, covering six sampling sites in total (figure 1). The AQEM protocol [6, 7] was applied and semi-quantitative sampling was performed by using a standard benthological hand net (25x25 cm, 500 µm mesh size). Samples were preserved using 60 - 80% ethanol solution and further processed in the laboratory for hydroecology and water protection of the institute for biological research „Siniša Stanković" in Belgrade. Identification to the lowest taxonomic level (preferably species level) for the main taxonomic groups was done by using appropriate taxonomic keys.

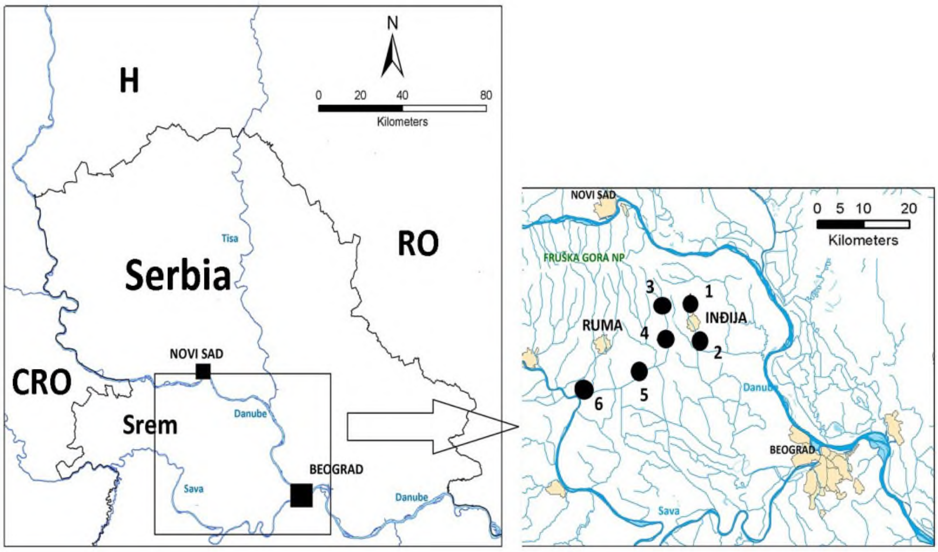

Figure 1. Investigated localities

In order to assess water quality and ecological status of investigated localities, the following metrics were used: total number of taxa, Zelinka and Marvan Saprobic Index [8], Biological Monitoring Working Party (BMWP) Score, ASPT-Average Score per Taxon [9], Diversity index H [10] and percentage participation of

Oligochaeta/Tubificidae in the total macroinvertebrate community. For saprobiological analyses, a list of bioindicator organisms according to Moog was applied [11]. The metrics calculation was performed using ASTERICS software [6]. Indicative status assessment was carried out according to the national legislation [5], based on the class boundaries for Type 5 watercourses (watercourses in the Pannonian plain, except the watercourses of Type 1).

RESULTS AND DISCUSSION

During our investigation a total of 80 macroinvertebrates taxa were determined. The majority of recorded taxa with known saprobiological preferences belong to α - mesosaprobic and β –mesosaprobic organisms, tolerating a certain degree of organic pollution.

The total number of taxa per sample ranged from 2 (sampling site 2 – downstream Inđija) to 37 (sampling site 1 – upstream Inđija) (table 1). Saprobic index (SI) ranged from 2.14 (sampling site 5) to 2.66 (sampling site 1). It should be noted that due to low number of taxa found and inadequate taxonomic resolution (family) this index was not calculated for two sampling sites (sampling sites 2 and 6). Values of BMWP and ASPT metrics ranged from 3 (sampling site 2) to 112 (sampling site 1) and from 1.5 (sampling site 2) to 5.43 (sampling site 4), respectively. Calculated values of H-diversity index ranged from 1.65 (locality 6 - Jarak) to 2.86 (locality 3 - Maradik downstream, Šelevrenac). It should be mentioned that for one locality (Inđija downstream) H-index could not be calculated (an only one taxon was found). Median value of used diversity index is high (2.17) and could points to diverse communities present along investigated watercourses. Taxa within class Oligochaeta and family Tubificidae were the numerous at the sampling site 6 (76.74 %) and sampling site 3 (64.65 %), while at the sampling site 4, no Oligochaeta were found.

Table 1. Values of indices used for water quality assessment at investigated localities

Locality	1	2	3	4	5	6
Number of Taxa	37	2	23	24	29	4
SI (Zelinka & Marvan)	2.66	/	2.45	2.39	2.14	/
BMWP	112	3	49	76	107	8
ASPT	4.87	1.5	4.08	5.43	5.35	2.67
H (Shannon-Wiener Index)	2.31	0	2.86	2.44	2.01	1.65
Oligochaeta [%]	20.81	33.33	64.65	0	12.11	76.74

Based on all used indices a very good (class I) and good (class II) water quality/ecological status, was recorded at three localities (sites 4, 5 and 1), while very low water quality (class V) was detected at localities 2 and 6 (table 2). Having in mind that the poorest water quality was found downstream larger settlements (Inđija and Ruma), it could be assumed that industrial and urban wastewaters represents the main treats to watercourses and their macroinvertebrates communities in this region. It should be noted that as only one seasonal aspect (an Autumn), was covered here, a prolonged investigation is needed for more reliable data.

Table 2. Water quality assessment of investigated localities based on biotic indices (according to 74/2011, type 5)

Locality	1	2	3	4	5	6
Number of Taxa	1	5	1	1	1	5
SI (Zelinka & Marvan)	3	/	2	2	2	/
BMWP	1	5	2	1	1	5
ASPT	2	5	2	1	1	4
H (Shannon-Wiener Index)	1	/	1	1	2	2
Oligochaeta [%]	2	3	4	0	2	5
ASSESSMENT	2	5	3	1	1	5

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REFERENCES

1. Živić, I., Marković, Z., Brajković, M. (2002). Macrozoobenthos of three brooks in the southern part of the Pannonian Plain: comparative analysis of secondary production. Tiscia 33: 37-44.
2. Cvetić, T., Sabovljević, M. (2005). A contribution to the bryophyte flora of Fruška Gora (Vojvodina, Serbia). Phytologia balcanica 11(1): 35-43.
3. Marković, V., Atanacković, A., Zorić, K., Ilić, M., Kračun-Kolarević, M., Tubić, B. (2014). Diversity of Aquatic Macroinvertebrates in Streams in the Belgrade Region (Does Different Stream Types Matter?). Water Research and Management 4(4): 39-45.
4. WFD (2000). Water Framework Directive – Directive 2000/60/EC of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy.
5. Official Gazette of the Republic of Serbia 74/2011. The parameters of ecological and chemical status of surface waters and parameters of the chemical and quantitative status of groundwaters.
6. AQEM Consortium (2002). Manual for the application of the AQEM system. A comprehensive method to assess European streams using benthic macroinvertebrates developed for the purpose of the Water Framework Directive. Version 1.0 (www.aqem.de), February 2002, 202 pp.
7. Hering, D., Verdonschot, P.F.M., Moog, O., Sandin, L. (2004). Overview and application of the AQEM assessment system. Hydrobiologia 516: 1-20.
8. Zelinka, M., Marvan, P. (1961). Zur Präzisierung derbiologischen Klassifikation der Reinheit fließenderGewässer. Arch.Hydrobiol. 57: 389-407.
9. Armitage, P.D., Moss, D., Wright, J.F., Furse, M.T. (1983). The performance of a new biological water quality score system based on macroinvertebrates over a wide range of unpolluted running-water sites. Water Research 17: 333-347.

10. Shannon, C. E. (1948). A mathematical theory of communication. The Bell System Technical Journal 27: 379-423.
11. Moog, O. (2002). Fauna Aquatica Austriaca. Katalog zur autökologischen Einstufung aquatischer Organismen Österreichs. Teil III, B, Metazoa. Bundesministerium f. Land- u. Fortwirtschaft, Wien.

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MULTI-CRITERIA ANALYSIS OF THE IMPACT INTERESTED PARTIES ON ACCESS TO SUSTAINABLE BUSINESS

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ABSTRACT

Access to sustainable business is of great importance to the satisfaction of stakeholders, and corresponds to modern trends and modern management.

The aim of this paper is to propose a methodology for evolving approach to sustainable business model based on stakeholders. From stakeholders depends the functioning of the organization and its survival.

The term sustainable business in economic theory is linked to sustainable development and implies adjustable economic social development, with respect for the principle of protection of the environment.

Consequently, the authors of this paper will analyze the influence of stakeholders on the approach to sustainable business by AHP (Analytical Hierarchy Process) method, one of the methods of multi-criteria analysis.

The resulting methodology contributes to most of the companies operating in the business models that are sustainable.

Key words: Stakeholders, Sustainable business, AHP method.

INTRODUCTION

In today's business world is increasingly mentioned the term "sustainable business" as relevant topic. In practice and literature the term "sustainable business" rapidly evolving. Getting adequate and appropriate model of sustainable business is difficult, due to the constant technological, economic and global changes. Stakeholders in the current business is important to achieve integration with sustainable development. It is interesting that the interests of stakeholders rapidly growing for sustainable business models. That literature data shows constantly grow in this field. Accordingly, that only some of the authors of a recent date: Boons et al (2013) [1], Bocken et al (2013) [2], Klein and its descendants al (2013) [3], Bocken and his colleagues (2014) [4] Miletic et al (2016) [5], and others. Papers authors Tukker and Tischner [6], and Wüstenhagen Boehnke [7], Kley and his associates [8], and Okkonen and Suhonen [9], show that the conceptual research sustainable business model is relatively new. Study Høgevold and Svensson (2014) [10], provides us with more knowledge and the real reasons for the establishment of a sustainable business model, which is important for interested parties.

Authors Høgevold and Svensson (2012) [11] give an explanation that sustainable business can be viewed as a continuous process. The biggest reasons for the establishment of sustainable business are the satisfaction of internal and external stakeholders. Sustainable business includes: a moderate and stable economic growth, satisfaction of stakeholders, social guarantees, successfully adapting to globalization, contribution to a healthy environment, proper use of natural and intellectual resources, maintaining cultural authenticity, Corporate Social Responsibility, eco-innovation and transformation consumption [5].

Accordingly, this paper discusses the influence of stakeholders on the approach to sustainable business. Stakeholders are groups or individuals who actively participate in sustainable business with their interests. Analysis of their interests is important for sustainable business and to win new markets, corporate responsibility, eco-innovation, environmental protection, reducing consumption and increasing profits.

The aim is that by applying appropriate methods determine the sequence of influence stakeholders on sustainable business, taking into account their individual requirements. These requirements represent their criteria where we rank them with respect to their analysis of their results. Analysis of the impact of sustainable business stakeholders determines the multi-criteria analysis.

Multi-criteria analysis or multi-criteria decision (MCDM) has many methods and techniques for the preparation of a suitable alternative. By these methods has the advantage that they at the same time considering the different criteria in the analysis process, such as financial and non- financial and qualitative and quantitative. MCDM methods use of the software that they allow rapid analysis for the particular field. The methods that are applied continuously in the literature are: AHP method (Analytical Hierarchy Process), SWARA, PROMETHE, ELECTRE, TOPSIS such as their combinations. The most famous software's are: Electra, Decision Lab, Expert Choice and Criterion Decision Plus.

In multi-criteria analysis is important a choice of method, but it is more important to the proper structuring of the problem, which includes the offered alternatives and defining the most important criteria for a specific problem [12] and [13].

To analyze the impact of stakeholders on sustainable business approach, AHP method has been chosen. Data methodology shows the order of influence peddling stakeholders on access to sustainable business, how many of the interested parties affects to the access of sustainable business. Applied methodology brings results which can increase sustainable business model evolution.

STAKEHOLDERS

The needs of the interested parties or stakeholders are different and constantly changing. In the present modern business role of stakeholders is important in strategic organization decision, environmental management and creation of model sustainable business. Stakeholders are groups or individuals with different specific interests with aim to preserve management resources and their potency. Their needs must be analyzed for achieving organizational objectives. Interested parties should not be seen as a homogeneous group rather as a heterogeneous with different requirements and needs.

In the analysis, stakeholders should identify, provide answers to essential questions such as: What are their relevant local interests and goals? What stakeholders expect from the organization? What can contribute to a particular process? What knowledge has? How informed? And finally, what are their motives to participate in a particular organization? In the final phase of stakeholder analysis should draft review their interest towards sustainable business? The results bring us a methodology for improving the quality of products and services and improve their prospects because they actively participate in the planning and management of sustainable business. Whether sustainable businesses survive or not, it depends on the stakeholders. Special attention to all interested parties is paid through constant contacts and cooperation. Interested parties are interrelated and they all have one common goal and that is profit. Developing a sense of differentiated stakeholders that depend on each other and that only together can achieve its goals, is one of the ways for a sustainable business. Stakeholders are integrate groups with different needs end expecting according to the association. They have interest for the different types of of activities in organizations.

Stakeholders of the sustainable business are:

Employees (criterion C1): Employed are a group of people who perform organizational activities in a profit of organization. Their needs and expectations are appropriate salaries for the relevant carried out activities. They are as interested parties wanting more money and that is reducing profits sustainable business. Employee satisfaction is the fulfillment of certain obligations of the organization and offer quality products and customer service.

Customers and consumers (Criterion C2): These stakeholders have maximum expectations from sustainable business. They expect faster delivery, satisfactory quality at a lower cost. For sustainable business costs are increases and revenue are decreases.

Vendors or suppliers (Criterion C3): As a sustainable business stakeholders want fast, accurate delivery of products and services, more efficient turnover of assets and a lower coefficient of receivables which requires greater consumption of sustainable business. With the increasing of supplier's costs and delivery the profit of sustainable business are reduced.

Syndicate (criterion 4): syndicate as the interested party as representative of the protection of interest, leads long lasting discussion with aim implementation of the employees' interest. Sustainable business has a loss because there is an interruption of business processes. These negotiations led to the suspension of work and to the dismissal of employees.

Manager's sustainable business (Criterion C5): Contemporary managers have to take all actions to solve conflict problems, which create the conditions to satisfy the users (customers), employees, syndicate, suppliers and the state. Modern management recognizes the need to function in a socially responsible manner and also designing and implementation of various quality systems [14]. Socially responsible behavior of modern managers and implementation of quality management system (QMS) together delivers: business to be sustainable, increase profitability, eco-innovation, economic and environmental sustainability. Based on this, sustainable business, evolving.

State (criterion 6): as an interested party or state apparatus has its own measures that contribute to increased taxes, thus ensuring self profit. In that case sustainable business has to their services and products cheapen, which contributes to the reduction of profits and survival.

Banks (Criterion C7): are the stakeholders of the organization which have an interest in charging credits and financial transactions. Through the organization of banks perform all business transactions: purchases of equipment, sale of goods and services, foreign trade, import and export of goods with the appropriate profit and carrying charge. Banks take big profits for financial transactions by reducing the prices for goods and services of organization. Accordingly, to sustainable business decreases profits.

ANALYSIS OF THE IMPACT INTERESTED PARTIES ON ACCESS TO SUSTAINABLE BUSINESS BY THE AHP METHOD

To analyze the impact of stakeholders on the approach to sustainable business AHP method was used for the calculation is used software Criterion Decision Plus.

AHP method is one of the widely known multi criteria decision methods created by the Saaty (1980) [15]. It breaks down a complex problem in a multi-criteria decision in multi-dimensional hierarchical structure of objectives and criteria [16]. About the competence of this method is the fact that the AHP method was studied and improved by many scientific papers at many international universities. Based on this, every year in her honor, an international conference ISAHP (International Conference on Analytic Hierarchy Process) are held and its application [17].

AHP method is used to determine the weight coefficients of the criteria, indicating the influence of each criterion in a sustainable business approach. This comparison is done in pairs, applying a table-matrix comparisons 1-9 Table 1. This process includes the following tasks:

- forming a matrix of comparison criteria and
- assessment of the degree of consistency in order to check the consistency of the process.

Table 1. Comparing scale of decision elements

Dominance	
Description	**Rating**
Equally	1
Poor domination	3
Strong domination	5
Very strong domination	7
Absolute domination	9
2, 4, 6, 8 are intermediate values	

After a criteria comparison, on the basis of Saaty procedures the weight coefficients are counted. After comparison, the degree of consistency is checked. The degree of consistency needs to have a value less than 0.1. Otherwise, they must reconsider the values that are entered in the comparisons matrix, because the consistency level should be below 0.1.

The next step is the formation of a comparison matrix using the scale provided in Table 1. Table 2 shows the matrix (dimensions 7x7) is obtained on the basis of empirical estimates of the decision maker (a team of experts) in order to determine the importance of each criterion for the determination of the most influential interested parties to access sustainable business.

With the help of software Criterion Decision Plus results are obtained and shown in Table 3.

Table 2. Matrix comparison of criteria

Criteria	C_1	C_2	C_3	C_4	C_5	C_6	C_7
C_1	1	1	2	3	1/2	5	9
C_2		1	1/3	1/5	1/2	2	1
C_3			1	2	1/3	1/7	2
C_4				1	1/9	2	1
C_5					1	7	9
C_6						1	1
C_7							1

Table 3. Results obtained by AHP calculation

Criteria	C_1	C_2	C_3	C_4	C_5	C_6	C_7
Weighting coefficients criteria	0.208	0.084	0.095	0.101	0.365	0.108	0.048
Consistency coefficient	0.094						

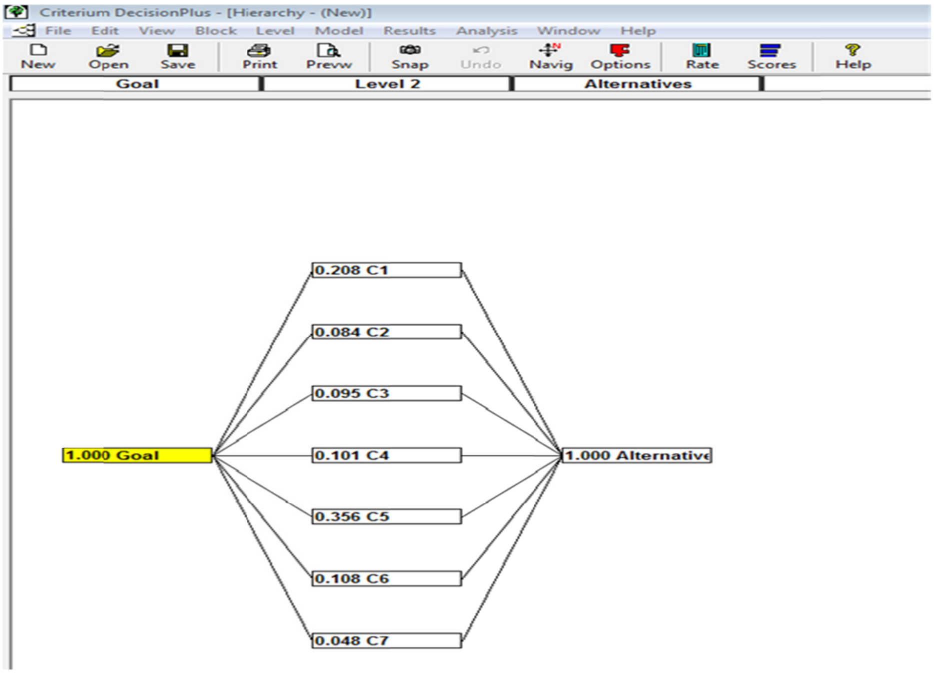

Figure1. Hierarchy influence stakeholders on access to sustainable business

Table 3 gives timetable of the impact of stakeholders on access to sustainable business and Figure 1 shows the hierarchy of their impact. Obtained results shows that the most influential stakeholder on approaches sustainable business are managers (C5) occupying the first place. The second place in the order of their impact occupying employed (C1), third state (6), a fourth syndicate (4), in the fifth place are the suppliers (C3), at the sixth are the customers (C2), and the seventh are the banks (7).

The first category includes managers (C5) that have the greatest impact on access to sustainable business of all stakeholders given because they have the highest value of weight coefficient of 0.356 obtained by analyzing AHP method. Consequently, they affect the 36.5% of access to sustainable business. Managers are the ones who must possess the necessary knowledge, skills and competence that will help them to quickly react to changes that occur in organizations with the aim of effective implementation of sustainable business [18].

The second category includes employees. Their weight coefficient is 0.208. That means that they have 20.8% impacts on access to sustainable business. Employees are those who perform organizational activities offering quality products and services to organizational profits for a fee. Employees are responsible for the functioning of the organization and to access sustainable business for the regular payment and job security.

A third category occupied state (6) with a weight coefficient of 0.108, and syndicate (4) which has a weight coefficient of 0.101. Their weights coefficients are approximate and their impacts on access to sustainable business are in the ranges from 10.1% to 10.8%. The state and syndicates act integrated in achieving a profit with aim of obtaining sustainable development.

The fourth category includes suppliers (C3) and customers (C2) as an interested party. The weight coefficient suppliers were 0.095, which means that 9.5% affect on access to sustainable business. Weight coefficient of customer is 0.084 means that affects the 8,4% on a sustainable business. Their influence values are approximate so that they operate integrated on sustainable business. From customers and suppliers also depend the functioning of the organization and approach to sustainable business with a percentage from 8.4 to 9.5%. Its requirements to reduce costs the profit of organizations will be reduced and the implementation of sustainable business will slowing down.

Fifth categories are the banks with the weight coefficient 0.048 (7) (Table 3). The impact on access to sustainable business of banks is 4.8%. AHP analysis shows that the banks take big profits from financial transactions that access to sustainable business decreases. The prices of products are decreases, services and transaction costs are increases and profit are decreases. Decrease of the profit lead to decrease sustainable business.

CONCLUSION

The article presents multi-criteria analysis of the impact of stakeholders on the approach to sustainable business by implementing AHP method. The applied methodology shows that managers (C5) belong to the first group of stakeholders and have the greatest impact on sustainable business approach and its implementation.

Obtained weight coefficient of 0.365 means that 36.5% influence on introduction of sustainable business.

The second group are employed which have influence 20.8% to access sustainable business, a third group comprising the state and syndicate with percentage impact of 10.1% to 10.8%, and the fourth group are suppliers and customers from 8.4% to 9.5%, and the fifth as well as the last group consists of the banks of 4.8%. The results show multi criteria analysis of the impact of stakeholders on implementation sustainable business. Sustainable business is the organization's efforts to properly manage economic, environmental, social, and cultural impacts and responses of stakeholders [19].

The applied methodology shows that very important for modern managers is to create a new concept of modern business, sustainable business that is considered dynamically and constantly process with great flexibility and adaptation. Sustainable models will give answers on different questions of interested parties with the help of modern management that has the purpose to quality managed and identifies their requirements.

Acknowledgment

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REFERENCES

1. Boons, F., Montalvo, C., Quist, J., Wagner, M., (2013). Sustainable innovation, business models and economic performance: an overview, *Journal of Cleaner Production* 45, Elsevier, pp. 1-8.
2. Bocken, N., Short, S., Rana, P., Evans, S., (2013). A value mapping tool for sustainable business modelling. *Corp. Gov.* 13 (5), pp. 482-497.
3. Klein, Barbara D., (2013). Elif Izberk-Bilgin; Charu Chandra; Hei-Wai Lee, A holistic approach to the scholarship of sustainable business , *Journal of Case Studies in Education,* 4, pp.1.
4. Bocken, N.M.P., Short, S.W., Rana, P., Evans, S., (2014). A literature and practice review to develop sustainable business model archetypes, *Journal of Cleaner Production* 65, Elsevier, pp. 42-56.
5. Miletić, S., Paunković, Dž., Mihajlović, D., Bogdanović, D., Đurić, M., (2016). Ilustracija modela održivog poslovanja rudarskih kompanija. *Ekologica* 23(82), стр. 360-365.
6. Tukker, A., Tischner, U. (Eds.), (2006). *New Business for Old Europe: Product-service Development, Competitiveness and Sustainability*. Greenleaf, Sheffield.
7. Wüstenhagen, R., Boehnke, J., (2008). *Businessmodels for sustainable energy*. In: Tukker, A., Charter, M., Vezzoli, C., Sto, E., Andersen, M.M. (Eds.),

System Innovation for Sustainability. Green Leaf Publising Ltd Sheffield, pp. 85-94.

8. Kley, F., Lerh, C., Dallinger, D., (2011). New business models for electric cars: a holistic approach. *Energy Policy 39*, pp. 3392-3403.
9. Okkonen, L., Suhonen, N., (2010). Business models of heat entrepreneurship in Finland. *Energy Policy* 38, pp. 3443-3452.
10. Høgevold, N.M. and Svensson, G., (2014). Sustainable business models: Corporate reasons, economic effects, social boundaries, environmental actions and organizational challenges in sustainable business practices, Baltic Journal Of Management , 9 (3), 357-380
11. Høgevold, N.M. and Svensson, G., (2012). A business sustainability model: a European case study, Journal of Business and Industrial Marketing, 27(2), 141-151.
12. Bufardi, A., Gheorghe, D., Hirouchakis, P., (2004). Multicriteria decision-aid approach for product end-of-life alternative selection. *International Journal of Production Research*, 42(16), pp. 3139–3157.
13. Mergias, I., Moustakas, K., Papadopolos, M., Loiyidou, M., (2007). Multi-criteria decision aid approach for the selection of the best compromise management scheme for ELVs: The case of Cyprus. *Journal of Hazardous Materials*, 147, pp. 706–717.
14. Dimitrijević, Lj , Vujičić, S., Dimitrijević, Z., (2012). Marketing and control of multiple stakeholders concerning the company. *International Scientific Conference MANAGEMENT 2012,* 158-164.
15. Saaty T.L., (1980). *The Analytical Hierarchy Process,* McGraw-Hill, New York, USA.
16. Lee W.B., Lau H., Liu Z., Tam S., (2001). *A fuzzy analytical hierarchy process approach in modular product design*, Expert System, 18 (1) 32-42.
17. Izet, H., (2014). Upravljanje izradom generalnih projekata u oblasti infrastrukture primenom višekriterijumske analiza. *Doktorska disertacija*, Univerzitet Novi Sad, Fakultet Tehničkih Nauka **.**
18. Urošević, S., Karabašević, D., Stanujkić; D., Maksimović, M., (2017). An approach to personnel selection in the tourism industry based on the swara and the waspas methods. *Economic Computation & Economic Cybernetics Studies & Research*, 51(1), p75-88.
19. Miletić, S., (2017). Implementacija metoda višekriterijumskog odlučivanja u održivom poslovanju rudarskih kompanija. *Doktorska disertacija,* Univerzitet " Džon Nezbit" Beograd, Fakultet za Menadžment u Zaječaru, str.13.

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MODEL OF ENVIRONMENTAL ASPECTS IMPACT ASSESSMENT BASED ON RISK ASSESSMENT IN FUNCTION OF EMS IN ACCORDANCE WITH ISO 14001

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ABSTRACT

Environmental management system of any organization must include all aspects of the environment that may have a significant impact on the organization objectives achievement. New standard ISO 14001: 2015 requires identification and analysis of environmental aspects on the basis of risks and opportunities analysis. Accordingly, in this paper is developed the methodology for determining the significance of environmental aspects on the basis of a risk assessment. Proposed model for the significance of environmental aspects evaluating is applied in the organization for the ceramic tile production, which is classified in the group of IPPC facilities. The applied methodology was the basis for the "Environmental management in the Keramika Kanjiža d.o.o design, in accordance with ISO 14001: 2015" which gave satisfactory results.

Key words: model, risk analysis, management, environmental aspects.

INTRODUCTION

New version of ISO 14001:2015 standard requires risk and opportunities determination related to the environmental aspects [16]. The adoption of ISO / IEC DIRECTIVE, ANNEX E [20] defines the structure of all future standards related to management systems, as defined by the content of the standard ISO 14001: 2015. An important novelty refers to the identification of external and internal risks [16] as a convenience for the development of the organization "based on the assessment and risk management." Accordingly, within the project "Establishment of environmental management system in Keramika Kanjiža d.o.o in accordance with ISO 14001: 2015" was developed and applied model for evaluating the impact of environmental aspects on the basis of risk analysis [8].

The aim of this research is to develop a simple and proactive model of evaluating the environmental aspects impact which, among other things, requires the standard ISO 14001: 2015. Keramika Kanjiža d.o.o is the IPPC facility and it is important to implement, maintain and improve an effective and efficient system of environmental management (*Environmental menagement system – EMS*).

Based on the research objectives, the following tasks were followed by:

1) defining context, concept and the flowchart of identification, impact evaluation and environmental aspects management;
2) development of criteria for evaluating the impact of environmental aspects;
3) implementation of the identification and evaluation of the environmental aspects impact;
4) selection of options for the treatment and management of aspects with a significant environmental impact.

For aim and tasks of research set this way, were used known research methods:

- the method of general systems theory and systemic approach,
- the method of theory and practice analysis, and
- descriptive methods of the process of production of ceramic tiles observation and description.

MODEL DEVELOPMENT

An effective system of environmental management includes proper identification, impact evaluation and management of environmental aspects by applying of appropriate management principles [16, 18]. To determine the significance of the environmental impact every single aspect of the environment, it is necessary to determine the level of environmental risk or risk priority index (RPI). Based on the determined environmental risk level is determined classification of impacts on the environment aspects significance.

Environmental aspect is an element of activities, products or services of an organization which is or may be in a reciprocal relationship with the environment [16]. The environmental aspect can cause an impact on the environment. Significant environmental aspect is one that has or may have one or more significant effects on the environment. Significant environmental aspects evaluated organization by applying one or more criteria

For evaluation of impact the environmental aspects in this paper is applied KINYY optimized method with specially defined criteria relevant to the determination environmental index priority risk.

Applying the guidelines of ISO 31000: 2015 [19] defined is the concept and flow diagram of evaluating the environmental aspects impact of the IPPC facility Keramika Kanjiža d.o.o, that is shown in the Figure 1.

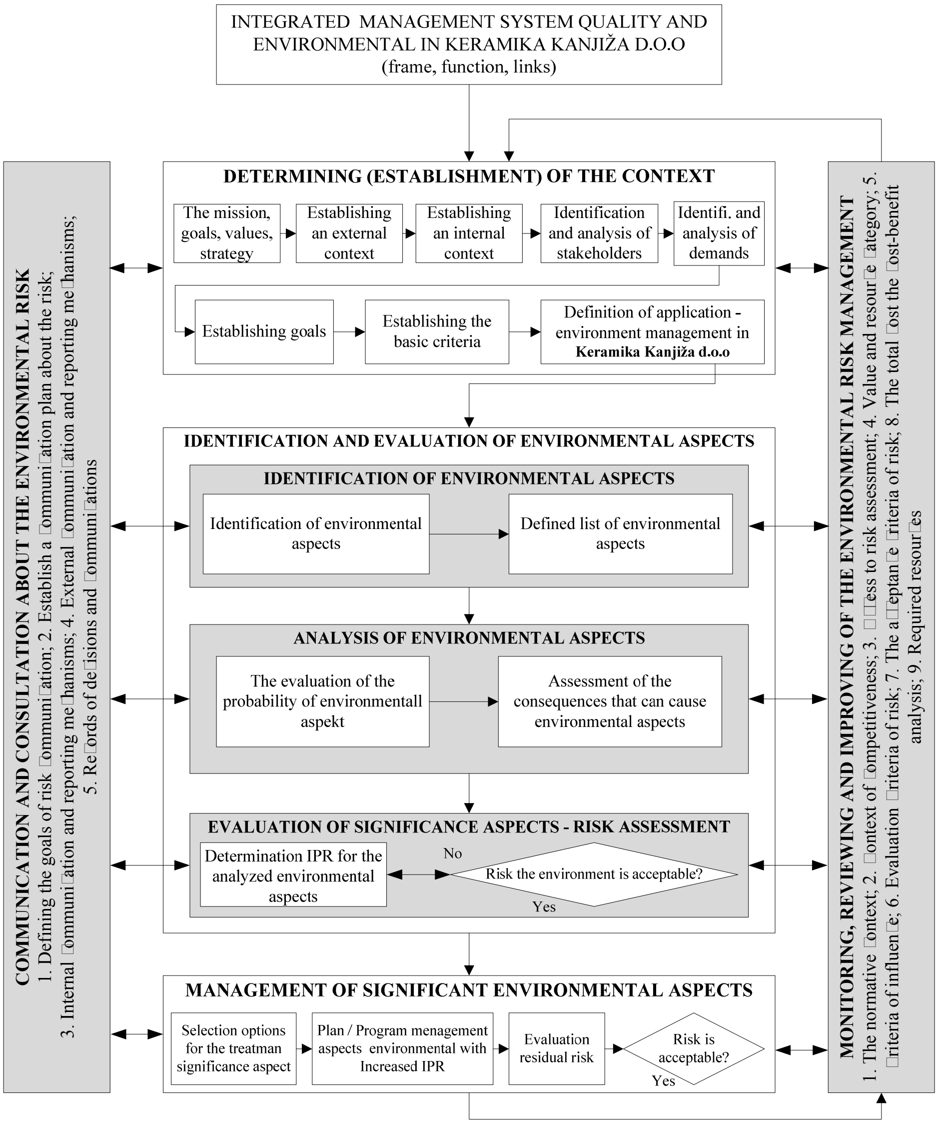

Figure 1. Concept and flow chart of the environmental aspects impact evaluating
Source: Adjusted by author, in accordance with the guidelines of the standard *ISO 31000: 2015* [19].

Optimization of KINNY method

One of the methods by which it is possible to make environmental aspects impact evaluation is the Kinny method. Aspects with a significant environmental impact and increased environmental risks priority index are changing over time through three basic categories that are analyzed by Kinny method:

- probability of environmental aspects occurrence;
- weight of the consequences that environmental aspect can cause;
- frequency of environmental aspects occurrence.

The main factors of the environmental aspects impact analysis are: V (probability), P (consequences), U (frequency) and RPI (risks priority index) that are expressed numerically, so the final evaluation of the environmental aspects impact significance is numerically expressed.

A basic setting of Kinny method is simple and easy to understand. The essence of the method lies in the realization of the following activities:

a) identification and determination of all environmental aspects that have or may have an impact on the environment;
b) analysis of each identified and established aspect with actual or potential impact on the environment in order to determine, by analytical methods,:
    - probability of environmental aspects occurrence;
    - weight of the consequences that environmental aspect can cause;
    - frequency of environmental aspects occurrence.
c) evaluation of the environmental aspect impact significance is made of three factors product:
    - probability of environmental aspects occurrence V;
    - weight of the consequences that environmental aspect can cause P,
    - frequency of environmental aspects occurrence U.
d) evaluation of the environment aspect impact significance is expressed through the risks priority index **- RPI** by formula:

$$\mathbf{RPI = V \times P \times U}$$

Criteria for probability of environmental aspects determining

Probability of environmental aspects occurrence (V) is ranking from 0,1 – It is not probable that environmental aspect occur, to 10 when the probability of environmental aspects occurrences are considered predictable and quite expected.

Table 1. Criteria description for probability of environmental aspects occurrence assessing

RANK	CRITERIA DESCRIPTION FOR PROBABILITY ASSESSING
0,1	It is **not probable** environmental aspect occurrence
0,2	It is **negligibly low probable** environmental aspect occurrence
0,5	It is **very low probable** environmental aspect occurrence
1	It is **low probable** environmental aspect occurrence
3	It is **probable occasional** occurrence of environmental aspect
6	It is **quite possible** occurrence of environmental aspects
10	**Predictable, expected** occurrence of environmental aspects

Criteria for weight of the consequences caused by environmental aspects assessment

Criteria for weight of the consequences caused by environmental aspects assessment (P) are ranked from 1 (negligible), to 10 (disastrous consequences), are listed in Table 2.

Table 2. Criteria description for weight of the consequences that can be caused by environmental aspects

RANG	CRITERIA DESCRIPTION FOR CONSEQUENCES ASSESSMENT
1	Expected are **negligible** consequences to the environment, which are manifested as discontinuous, short-term, episodic pollution of the environment, that are significantly below the the permitted levels, and affect or may affect only on the installations.
2	Expected is **small** impact on the environment, which is manifested as continuous pollution of the environment that does not exceed maximum allowed value and MAC (maximum allowed concentration), and affect or may affect on equipment and / or industrial circle.
3	Expected are **increased** consequences to the environment, which are manifested as continuous environmental pollution that exceed maximum allowed value and MAC (maximum allowed concentration), and affect or may affect outside the limits defined by environmental system. May be required temporary interruption of work.
6	Expected are **great** consequences to the environment, which are manifested as continuous environmental pollution that several times exceed maximum allowed value and MAC (maximum allowed concentration), and affect or may affect outside the limits defined by environmental system and the wider community. Request a temporary interruption of the work process and prevention or remediation of pollution.
10	Expected are **very large** consequences to the environment, which are manifested as continuous environmental pollution that several times exceed maximum allowed value and MAC (maximum allowed concentration), and affect or may affect outside the limits of a defined by environment system and have or may have an international (cross-border) impact on the environment. It is understood an immediate end of working process and prevention and / or recovery of the pollution.

Criteria for frequency of environmental aspects occurrence assessing

Criteria for assessing the frequency of environmental aspects occurrence (U) are ranked from very rare (1) to permanently or continuously (10) environmental aspects occurrence as shown in the Table 3.

Table 3. Criteria description for the environmental aspects occurrence frequency

RANK	CRITERIA DESCRIPTION FOR FREQUENCY
1	*It appears very rarely (per year)*
2	*Appears monthly*
3	*Appears weekly*
6	*Appears daily*
10	*Appears continually and daily*

Criteria for determining the environmental aspects impact significance

The significance of the environmental aspects impact is expressed through the risk priority index (RPI) and ranks from acceptable or slight to extreme and unacceptable risk to the environment, that requires interruption of operational activities and instantaneous undertaking of corrective action.

Table 5. Criteria for determining the environmental aspects impact significance

RPI	Environmental risk classification	Environmental risk characterization	Categorization of environmental aspects impact significance	Description of environmental aspects impact significance
≥ 0,1 ≤ 20	*Negligible risk*	*Acceptable risk*	*Very poorly significant environmental aspect*	Does not identify the need for special treatment, just routine application of preventive measures that assessed risks to the environment maintained at an acceptable level.
≥ 21 ≤ 70	*Low risk*	*Acceptable risk*	*Poorly significant environmental aspect*	Does not identify the specific need for treatment, but only implementation of routine preventive measures, monitoring and measurement primary environmental quality factors in order to maintain environmental risk within the acceptable level.
≥ 71 ≤ 200	*Increased risk*	*Conditionally acceptable risk*	*Significant environmental aspect*	Does identify the specific needs for treatment, development of special plans and programs for the implementation special remedial measures and increased monitoring to reduce the environmental risk to an acceptable level.
≥ 201 ≤ 400	*Great risk*	*Unacceptable risk*	*Very significant environmental aspect*	Mandatory is a treatment by applying special plans and programs for the implementation of special remedial measures and increased monitoring and measurement to reduce environmental risks to an acceptable level. Consider the need for temporary break of operations and the need for urgent application of the additional corrective measures that will impact on reducing the risk to an acceptable level. It is necessary to carry out continuous supervision and monitoring of the primary environmental factors. If necessary, make a new evaluation of the environmental aspects impact.
≥ 400 ≤ 1000	*Very great risk*	*Unacceptable risk*	*Exceptionally significant environmental aspect*	Mandatory is use of special treatment plans and programs for the implementation of specific corrective measures, and increased monitoring of the primary environmental factors to reduce environmental risks to an acceptable level. Consider the need for urgent break of operations, with mandatory application of additional corrective measures that will impact on reducing risk to an acceptable level. It is necessary to carry out continuous supervision and monitoring of basic environmental factors. Execute new evaluation of the environmental aspects impact and define new measures for risk management in the environment.

Model of environmental management in Keramika Kanjiža

In accordance with the requirements of ISO 14001: 2015 defined is the following integrated model for management of product and service quality and significant environmental aspects [8] [16] [18].

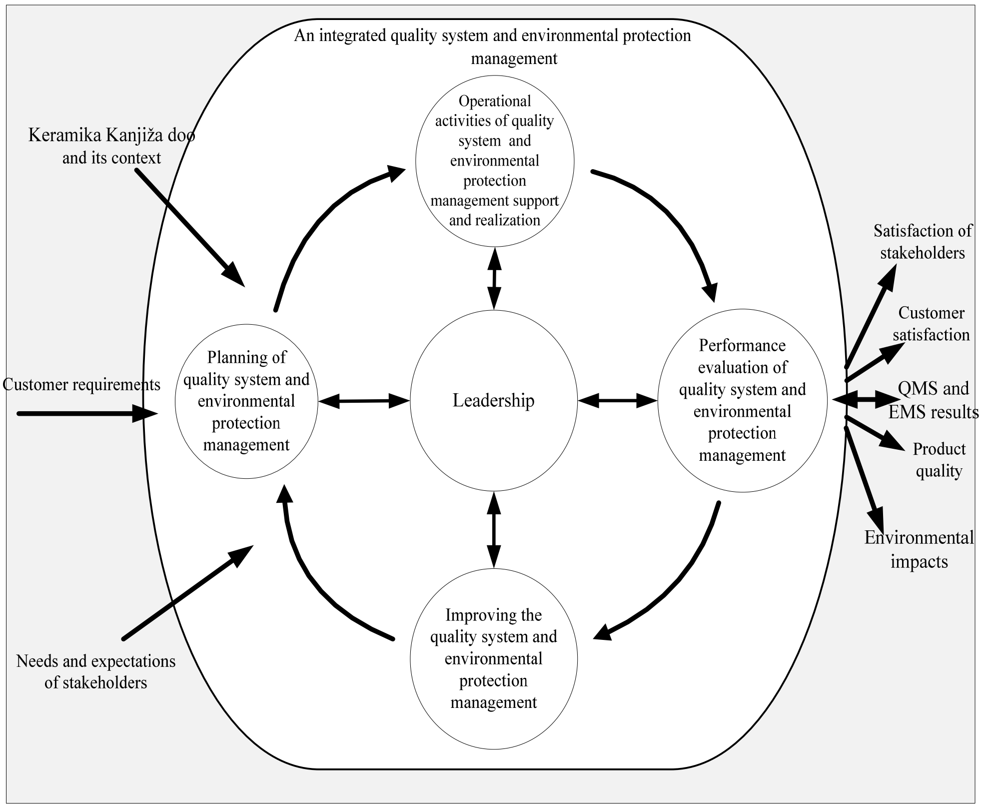

Figure 2. Model of integrated management system QMS and EMS in Keramika Kanjiža d.o.o

MODEL IMPLEMENTATION – CASE STUDY

A brief description of the site and facilities for the ceramic tiles production

Keramika Kanjiža d.o.o whose activity is ceramic tiles and decorative accessories manufacturing, in the main process has a number of operational activities that have or may have a significant impact on the environment. Keramika Kanjiža d.o.o is, based on the type of activity and production capacity, by the decision of the competent national authority, classified as IPPC installation [22]. Consequently, it was necessary that Keramika Kanjiža d.o.o develop its own concept of the impact assessment and management by aspects with high environmental risk in order to establish, implement, maintain and improve the environmental management system.

Kanjiža settlement is located on the right bank of the river Tisza, on the northern part of the Republic of Serbia. It borders with River Tisza and the Novi Kneževac municipality from the east, with Senta municipality from the south, with Subotica municipality from the west, and with Serbian-Hungarian border from the north. IPPC facility Keramika Kanjiža d.o.o is located in the northern part of settlement Kanjiža, on the way to Horgoš, Subotica and the Serbian-Hungarian border. Distance from the manufacturing plant to the first residential buildings on the south is about 300 m.

The basic raw components that participate in operational activities are clay and feldspar, and for glazes are frit, kaolin and ceramic colors (so-called engobe earth-color or metallic pigments mixed with minced clay). Keramika Kanjiža d.o.o applied technology of single continuous firing of ceramic tiles, while the order of process is conducted according to the scheme shown in Figure 2 .: reception and storage of raw materials; preparation of ceramic mixtures; atomisation; pressing; drying; glazing; baking; sorting and packing of the finished tiles.

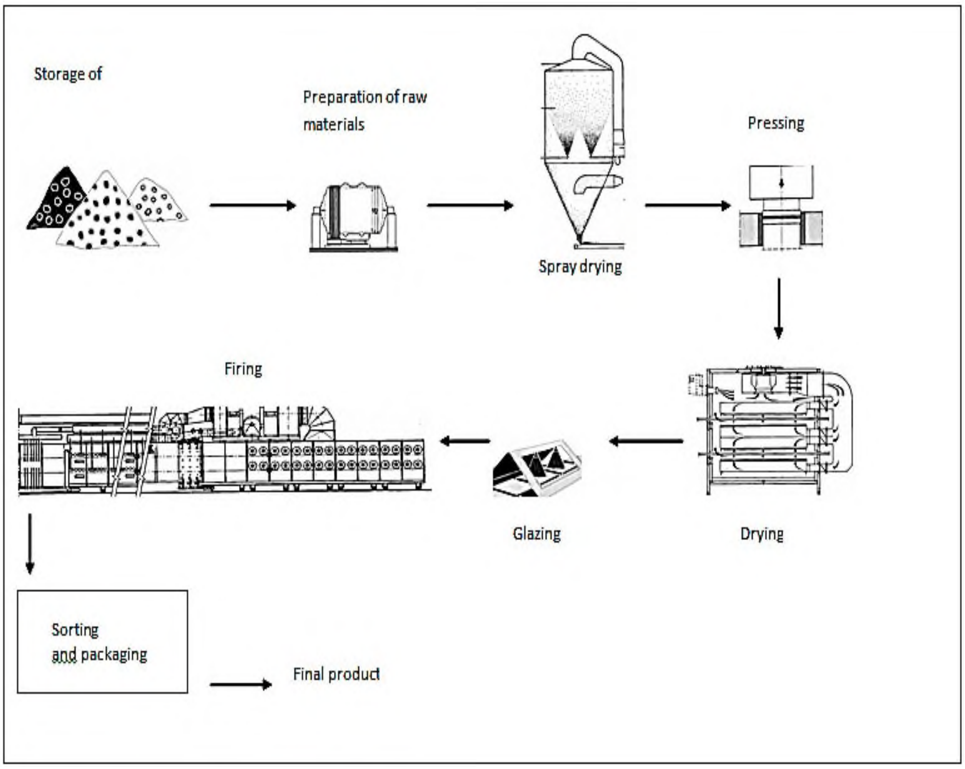

Figure 2. A simplified scheme of the ceramic tiles production process [8].

Receiving and storage of raw materials takes place outdoors. Clay is by loader inserted into the box-feeder that supplies a plant for crushing and homogenization of clay. Grinded clay is by tracks entered into boxes. Preparation of raw material mixture is carried out after preparation of appropriate amounts of clay. Based on the recipe from the laboratory a mixture of the total weight of 14 tons is prepared. The prepared mixture is moving by transporter system and loaded in the mills for wet grinding. Upon completion of this stage obtained is a ceramic intermediate sludge that is directed into the underground sedimentation tank. During this time, the homogenization occurs using piston pumps, and then under high pressure sludge is transported to the atomizer. The atomization of ceramic mass is a process of drying by spraying. Drops of certain dimensions by spraying are formed in a stream of hot air and fall to the bottom, from where in the form of granules are transferred by elevator in the storage silos, where they remain at least 24 hours to homogenise the moisture. After homogenization, the granulate is transported to the vibrating sieve, and then to hydraulic presses. Pressing is done by using hydraulic presses. Pressing leads to consolidation of granulate and formation of the crude product in the form and dimensions of the mold. After pressing, formed crude plates are entered into the dryer using conveyor belts. For the drying process is commonly used single channel horizontal kiln with blowing of hot air at 200 ° C. The drying process takes approximately 12 minutes. The moisture content of the raw tiles after leaving the drying chamber is about 0.5% and the temperature is about 85 ° C. After drying, the tiles are transferred to the line for glazing and decorating. Firing is the final stage in the high temperature at which tiles retains its shape with a certain shrinkage and receives its final characteristics. For this phase are used kilns for firing with a fast firing cycle of 50 minutes at a temperature of 1110 ° C or 40 min at 1190 °C. Temperature regime includes three zones: preheating, firing and cooling. After firing, tiles are lining up automatically on a metal platform, and then transported by forklift to the sorting line, where control and classifying the product takes place. After sorting they are packed in cardboard boxes of standard dimensions, and then on pallets, which are coated with thermo-shrink wrap. Finished pallets are transported by forklift truck into a warehouse. The current daily capacity is 100,000 m^2 of finished product, 3,000,000 m^2 per year or 140 tonnes per day.

Environmental impact of aspects evaluating

Technological process of ceramic tiles and decorative accessories production consist of the following operations: (1) supply and storage of clay, (2) prepare the clay for the production of ceramic tiles; (3) grinding the clay; (4) ceramic mixture atomization; (5) pressing; (6) drying; (7) glazing; (8) **firing**; (9) sorting; (10) decorative accessories; (11) processing of waste tiles; (12) maintenance of infrastructure (13) maintenance of transport equipment; (14) maintenance of industrial hygiene.

For the purposes of this article and checking the effectiveness of the proposed model of evaluation environmental aspects impacts, as example is taken one of the most important operations of technological processes (8) **firing** of ceramic tiles.

Step 1. Identification and determination of environmental aspects

Table 6. Identification and determination of environmental aspects

Organizational unit:	**Sector - Manufacturing**	
Step 1	**Identification of environmental aspects**	
Name of plan, program, project, process, activity or operation:	**Identified environmental aspect**	**Actual or potential impact of the identified environmental aspects**
(8) Ceramic tiles firing	Floor and wall tiles firing	Capacity of kiln for ceramic tiles firing (Note: kiln capacity exceeds 4 m^3 and charge density per kiln exceeds 300 kg / m^3, so authorities rank this factory among the IPPC installation [22])
		Potential occurrence of fire and explosion due to use of liquefied petroleum gas in the firing stage of floor and wall tiles
		Emission of large quantities of waste heat from firing phase of floor and wall tiles.
		Potential air pollution in the environment by emission of particulate matter with content of NOx, COx and so on., from floor and wall tiles firing stage
		Industrial waste generation from the floor and wall tiles firing phase.

Step 2. Analysis of identified environmental aspects

After performed identification the access to the analysis of the identified environmental aspects is possible, in accordance with the adopted criteria shown in Tables 1 - 5.

Step 3. Environmental aspects significance evaluation- risk assessment

Based on established criteria for environmental aspects probability, potential weight of consequences that environmental aspects may cause, and frequencies of the environmental aspects occurrence, the risk priority index - RPI is determined, or risk to the environment and environmental aspects impact significance.

Table 7. Environmental aspects significance determination and analysis

Organizational unit:	**Sector – Cramic tiles manufacturing**				
Name of plan, program, project, process, activity or operation:	**(8) Ceramic tiles firing**				
Step 2. Analysis of determined environmental aspects	**Step 3. Risk priority index determination and environmental aspects importance clasification**				
	Probability	**Consequence**	**Frequency**	**RPI**	**Environmental aspects importance clasification**
The actual or potential impact of the identified environmental aspects	**V**	**P**	**U**		
Capacity of ceramic tiles firing kiln (Note: with a kiln capacity exceeding 4 m^3 and with a density per kiln exceeding 300 kg / m^3 authorities ranks this factory among the IPPC installation)	10	3	10	300 Great risk	***Very important environmental aspect***
The potential occurrence of fire and explosion due to the use of liquefied petroleum gas in the firing stage of floor and wall ceramic tiles - a potential accident or emergency situation	3	9	10	90 Increased risk	***Important environmental aspect***
The emission of large quantities of waste heat from the firing stage of floor and wall ceramic tiles.	10	2	10	200 Increased risk	***Important environmental aspect***
Potential environmental air pollution by emissions of particulate matter with content of NOx, COx and so on., from the stage of floor and wall ceramic tiles firing	10	3	10	300 Great risk	***Very important environmental aspect***
Generating of industrial waste from the firing stage of floor and wall ceramic tiles.	10	3	3	90 Increased risk	***Important environmental aspect***

Table 8. Register of significant environmental aspects of operation -firing

No.	**Name of plan, program, project, process, activity or operation:**	**Important environmental aspect**	**RPI**
(8)	**Ceramic tiles firing**	Capacityof ceramic tiles firing kiln (kiln capacity exceeding $4m^3$, with a density per kiln exceeding 300 kg / m^3)	300
		Potential environmental air pollution by emissions of particulate matter with content of NOx, COx and so on., from the stage of floor and wall ceramic tiles firing	300
		The emission of large quantities of waste heat from the firing stage of floor and wall ceramic tiles.	200
		The potential occurrence of fire and explosion due to the use of liquefied petroleum gas in the firing stage of floor and wall ceramic tiles - a potential accident or emergency situation	90
		Generating of industrial waste from the firing stage of floor and wall ceramic tiles.	90

Step 4. Management of aspects with a significant environmental impact

For all aspects with a significant impact on the environment options for treatment are selected and plans and programs for the establishment mechanisms of control over aspects with a significant environmental are defined. impact.

Table 9. Management of aspects with a significant environmental impact

Step 4:	**Management of aspects with a significant environmental impact**			
Name of plan, program, project, process, activity or operation:	**Aspects with a significant environmental impact**	**RPI**	**Selection of options for treatment / handling with significant environmental aspects**	**Plans and programs for significant environmental aspects management**
(8) Ceramic tiles firing	Capacityof ceramic tiles firing kiln (kiln capacity exceeding 4m^3, with a density per kiln exceeding 300 kg / m^3)	300	The application of organizational and technical measures of control	Compliance with legal and other requirements and obtaining integrated permit (IPPC permit)
	Potential environmental air pollution by emissions of particulate matter with content of NOx, COx and so on., from the stage of floor and wall ceramic tiles firing	300	The application of organizational and technical measures of control (monitoring)	Drafting the monitoring and measurement plan and program of emissions particulate matter with content of NOx, Cox... Compliance with the BREF documents, and application of best available techniques - BAT
	The emission of large quantities of waste heat from the firing stage of floor and wall ceramic tiles.	200	The application of organizational and technical measures of control (monitoring)	Drafting the energy efficiency plan and program; Compliance with the BREF documents, and the application of best available techniques - BAT
	The potential occurrence of fire and explosion due to the use of liquefied petroleum gas in the firing stage of floor and wall ceramic tiles - a potential accident or emergency situation	90	The application of organizational and technical measures of control (monitoring)	Drafting the Plan for dealing with emergencies. Obtaining approval from the competent authority for the present plan.
	Generating of industrial waste from the firing stage of floor and wall ceramic tiles.	90	The application of organizational and technical measures of control (monitoring)	Plan and program of waste management in IPPC facility

DISCUSSION

This paper presents a model for evaluating significance of the environmental aspects impact, and establishing mechanisms of control over aspects with a significant environmental impact based on the environmental risks analysis and evaluation. From the report on the evaluation of the environmental aspects for IPPC facility Keramika Kanjiža d.o.o [8] for this study is shown only one operation of the technological process - ceramic tiles firing. Based on detailed identification and analysis performed for all 14 operations of the technological process in the IPPC facility Keramika Kanjiža d.o.o., there are identified and analyzed 65 environmental aspects of which 20 are evaluated with IPR $\geq 21 \leq 70$, 45 are evaluated with IPR $\geq 71 \leq 200$ and $\geq 201 \leq 400$, and classified as **important** and **very important environmental aspect**. Only for technological operation - firing ceramic tiles were identified three (3) important and two (2) very important environmental aspects.

For all identified important and very important environmental aspects, such as in the example given in Table 9., are defined corresponding plans/programs for the management of significant environmental aspects. In this way, for all the important environmental aspects with an increased environmental risk, are established mechanisms of control and environmental risk is reduced to an acceptable level.

Significance of the proposed model for evaluating the environmental aspects impact is that the leadership of Keramika Kanjiža d.o.o has the ability to make rational decisions regarding the planning, establishment, maintenance and improvement of the environmental management system and sustainable development.

In applying this model for environmental aspects impact evaluating, it is necessary that team for determining significance of these environmental aspects is multidisciplinary and consists of experts with specific knowledge in the field of ceramic tiles production, engineering and environmental management.

In the past, for the identification, analysis and evaluation of the environmental aspects significance are different concepts used without special attention to the analysis and evaluation of environmental risks. For most authors [1, 2, 3], today is prevailing opinion that for the evaluation of the aspects impact, as well as for the management of environmental aspects significance, is necessary to apply experience gained in practice, in order to meet the requirements provided by standards ISO 14001: 2015 and ISO 31000: 2015 .

CONCLUSION

In the case of the applied valuation model of the environmental aspects impact in the IPPC installation Keramika Kanjiža for only one technological operation (8) firing of ceramic tiles can be concluded that the proposed model has fulfilled the purpose and has given satisfactory results. The management of significant environmental aspects with increased risks for the environment in accordance with the proposed model fully meets the recommendations and guidelines defined by the standards ISO 14001: 2015 and ISO 31000: 2015. The proposed model fully respects the requirements of ISO 14001: 2015 relating to the evaluation of significant environmental aspects on the basis of risks and opportunities.

Evaluation of the environmental aspects significance on the basis of the proposed model enables that information about significant environmental aspects are adequately processed and used in decision-making at all relevant levels in the organization Keramika Kanjiža d.o.o.

Based on this proactive and comprehensive model of evaluating the environmental aspects impact as is defined in this paper, the management organization Keramika Kanjiža d.o.o is:

- accepted and approved the policy of environmental management [23];
- informed all interested parties about their aspects with a significant impact on the environment [23];
- defined mechanisms of control aspects with a significant environmental impact based on risk assessmentthat correspond to its performance [6];
- provided the distribution of necessary resources for the management of significant environmental aspects;
- provided compliance to requirement of standard SRPS ISO 9001: 2015 and SRPS ISO 14001: 2015 [16] [19];
- provided compliance with laws and regulations regarding environmental protection and obtained integrated permit (IPPC permit) from the competent authority [12];

The proposed model of evaluating the environmental aspects impact can be applied in other organizations with the same or similar activities that wish to plan, establish, maintain and improve its system of environmental management alone or in combination with other systems of quality management, health and safety at work and etc.., because it is based on the analysis, assessment and management of risks.

REFERENCES

1. Australian Government 2007d, Environmental Risk Assessment Guidance Manual for Industrial Chemicals (in draft), Environment Protection Branch, Department of the Environment and Water Resources, 2007.
2. Canada National Standard/Canadian Standards 2000, CAN/CSA Q850-97, Risk Management: Guideline for Decision Makers, Canada, Canadian Standards Association.
3. Lerche, I., Environmental risk assessment: quantitative measures, anthropogenic influences, human impact, Berlin, Springer, 2006.
4. Health and Safety Risk Management Manual for the Australian Coal Mining Industry 2007.
5. EMS Keramika Kanjiža; Proceeding PR-0-03 The management of risks and opportunities; 2016
6. EMS Keramika Kanjiža; Proceeding PR-0-04 Identification management and evaluation of the environmental aspects significance. 2016

7. Mrazovac – Kurilić S, N. Staletović, A. Salkai; Quantitative analysis of emissions from the production process Keramika Kanjiža; III Scientific conference with international participation Politehnika - 2015; Belgrade 2015
8. Project "Establishing a system of environmental management in Keramika Kanjiža d.o.o in accordance with ISO 14001: 2015" - The report on the identification and evaluation of environmental aspects; Keramika Kanjiža d.o.o; 2016
9. Rio Tinto 2005, Risk Analysis and Management Guidance, June 2005.
10. Decision on certification of EMS in accordance with SRPS ISO 14001: 2015 No. R-E-0428 from 16.11.2016. issued by the certification body YUQS d.o.o Belgrade
11. Decision on certification of QMS in accordance with SRPS ISO 9001: 2015 No. R-Q-1472-IIR-1 from 16.11.2016. issued by the certification body YUQS d.o.o Belgrade
12. Decision on integrated permit granting; R. Serbia, AP Vojvodina; Provincial Secretariat for Urban Planning and Environmental Protection; No. 130-501-1400/2011-06 from 15.12.2016.;
13. Staletović, N., "Development of assessment methods and environmental risk management model for the sustainable development", University in Novi Sad, 2006.
14. Salkai A, N. Staletović, S. Mrazovac – Kurilić; Assessment of the energy efficiency of the production process in Keramika Kanjiža; III Scientific conference with international participation Politehnika - 2015; Belgrade 2015
15. Staletović N., A. Salkai, S. Mrazovac – Kurilić; Modern principles of treatment, purification and reuse of process water in the production process of ceramic tiles in Keramika Kanjiža; III Scientific conference with international participation Politehnika - 2015; Belgrade 2015
16. Standard SRPS ISO 14001: 2015 - System of environmental management - Requirements.
17. Standard SRPS ISO 14031: 2005 - Environmental management - Evaluation of environmental performance - Guidelines
18. Standard SRPS ISO 9001: 2015 - Quality management systems - Requirements.
19. Standard SRPS ISO 31000: 2015 Risk management - Principes and guidelines.
20. Standards ISO/IEC Directives, Part 1, Consolidated ISO Supplement, Appendix 2; 2015
21. The World Bank (1997). Environmental hazard and risk assessment, p.2. Retrieved from http://siteresources.worldbank.org/INTSAFEPOL/1142947-1116493361427/20507357/ Update 21 Environmental Hazard And Risk Assessment December1997.pdf. (August 2011).
22. The Law on Environmental Protection ("Official Gazette of RS", no.134/04; 36/09; 72/09; 43/11).
23. www.keramikakanjiza.com

"TIMOK SCIENTIFIC TORNADO - TNT" - A MODEL FOR SCIENCE POPULARIZATION AND THE DEVELOPMENT OF COMPETENCIES THROUGH COOPERATION WITH THE STAKEHOLDERS

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ABSTRACT

"Timok Scientific Tornado – TNT" is a complex project that is being implemented for five years in Eastern Serbia. The aim of project is to contribute the reform of the educational system by developing specific extracurricular models and activities for popularization of natural and technical sciences, increase the knowledge and motivation of students for further education in these areas, develop the skills and competencies of students and teachers, raise environmental awareness, strengthen cooperation between schools and the surrounding stakeholders. Project activities include realization of the Science Festival, the Night of the Researchers and various scientific exhibitions. Due to the great success of previous events of such kind and the constant increase in the number of participants and demonstrations it is expected that the programs of the TNT will become part of the annual work plans of primary and secondary schools, and that all municipalities in Eastern Serbia become participants in this program.

Key words: Scientific caravan, popularization of science, science festivals.

INTRODUCTION

Strategy for development of Education in Serbia and other strategic documents refer to the need for reforming education not only within schools but also through cooperation of schools and all relevant actors (stakeholders) in the region [1]. At the same time, the decline of students' motivation for the realization of the classical school curricula (especially in the field of natural and technical sciences) is noticed, accompanied by increased interest for various forms of extracurricular programs and activities. Schools are unable to meet these interests without cooperation with the other schools and the wide range of different stakeholders outside the schools: civil society organizations (CSO`s), various institutions and companies, the media and others. Formal school education does not substantially contribute to the development of students and teachers competencies, nor it opens enough space for innovative teaching methods, implementation of ICT, or creates linkage with the surrounding stakeholders. Schools are lacking well-equipped laboratories for conducting the experiments in the field of natural and technical sciences. At the same time, the Science Festival and the Night of the

Researchers are being realized in Belgrade and other major cities as similar type of programs, but they are inaccessible to the majority of students and teachers from Eastern Serbia.

The newly adopted Strategy of Scientific and Technological Development envisage promotion of science through campaigns and actions as one of the priorities. They will be implemented by the interested institutions and organizations of civil sector in order to ensure the encountering of students with new or innovative approaches to learning and mastering scientific methodology [2]. National Strategy for Youth in Serbia provides a range of activities in education and training of young people, the development of youth competencies in the process of lifelong learning, leadership development programs, youth activism support, and health promotion programs [3]. New course in development of the civil sector suggests that CSOs should strengthen their role and involvement in formal education in cooperation with schools, as well as their participation in non-formal education and lifelong learning.

Scientific caravan TNT is designed to gather all interested stakeholders in order to contribute to the solutions for problems of educational reform, the science popularization and the lack of youth activism, in order to meet new needs of students and teachers, and to help in implementation of strategic documents in the fields of education, science and youth activities in municipalities of Eastern Serbia. The project includes the preparation and realization of scientific events (the Night of the Researchers and Science Festival) and scientific exhibitions (in Bor, Zajecar, Negotin, Knjaževac). These scientific events are conducted through scientific demonstrations and experiments and presentation of diverse scientific achievements. Their main task is to promote education in the field of natural and technical sciences, affecting the increase of knowledge in these areas, to develop the skills and competencies of students and teachers, raise environmental awareness, strengthen partnership and cooperation between educational institutions and the surrounding stakeholders.

As an innovative and a partnership program of science popularization, this project contributes in solving various problems in the reform of education and science by linking them with other sectors (culture, environment, civil society), by connecting schools with their local and regional surrounding, contributing to professional orientation and providing support to talented students and peer educators.

MATERIALS AND METHODS

Strategic documents relating to education, science, youth and CSOs were used as a base for designing Scientific caravan as an innovative model of education. Questionnaires for different target groups and reports of organizers (containing the data on number of participants and visitors, the number and variety of demonstrations, quality activities, degree of media coverage) were conducted as the evaluation tool for the planned targets of each activity. In an adaptive manner, monitoring and evaluation results are annually used for further improvement of the program.

RESULTS AND DISCUSSION

The project "Timok Scientific Tornado - TNT" has been implemented in the municipalities of East Serbia since 2012. The project is supported by the Ministry of Education, Science and Technological Development, Ministry of Agriculture and Environmental Protection, Ministry of Youth and Sports and the Center for the Promotion of Science through call for support of educational activities for CSO`s. Around 60 institutions from the area of education, culture, professional, public and commercial, as well as other CSO`s from East Serbia are included in the realization of this project [4]. Schools from Bulgaria and Romania also joined the project.

The project objectives are:

- development of applicable model for extracurricular activities of students and teachers in the field of natural and technical sciences;
- promotion of peer learning and active participation of students in the education of the wider population and the science popularization;
- fostering the potentials and talents of students;
- service of professional orientation and strengthening the motivation of young people for further education in the field of natural and technical sciences;
- promotion of mutual school partnerships with the participation of CSOs and other institutions and organizations;
- improving the competencies of teachers and students: work planning, organization and learning, interaction, thinking and reasoning skills, competences for lifelong learning, communication, work with data and information, problem solving, cooperation, environmental competencies, and individual competencies for health care, life in a democratic society, aesthetic and entrepreneurial competence, organizing, processing and presentation of data, secure electronic communication, using social networks for educational purposes, readiness to accept new ICT technologies, etc.
- improving the competence of teachers for teaching-oriented learning, monitoring trends in natural and technical sciences, application of the principle of obviousness and applicability (because of it`s importance to improve the content and outcomes of the educational process, which is base orientation of modern education). Special support is achieved by positioning teachers in the role of facilitators that guide the process of learning to students with diverse interests and abilities.
- promotion of additional extracurricular learning programs: Green package, the Danube Box, and similar.

Primary target groups are students of preschool, primary and secondary schools in the municipalities of Bor, Zaječar, Negotin, Kladovo, as well as their teachers. Secondary target groups are students and university professors as promoters of natural sciences and motivators for development of the innovative capacity of children and young people, scientific experts, experts from cultural and other professional institutions, experts from non-governmental organizations dealing with education, company representatives that may present their technologies and innovations. Target groups are also the visitors of scientific events as well as media through which the additional objectives of the project are achieved.

Innovativeness of the project is reflected in the correlation of advancement in knowledge, skills and competencies of different target groups (students, teachers, various experts). Through a collaborative and interactive learning student/teacher, pupil/student and teacher/ teacher the final selection of themes, experiments, demonstrations and presentations is achieved, as well as a multidisciplinary approach to specific topics. Other institutions and organizations from the local community and beyond show experiments, demonstrations and presentations of their working programs with youth, while and high schools and faculties perform practical experiments, demonstrations and presentations, promoting their educational profiles for the purpose of professional orientation. In particular, the inventiveness of the project is reflected in the fact that all the mentioned objectives are integrated into one unit which provides a synergy of these effects.

Main groups of project activities:

1. **Preparation of the organizers, educational institutions and other institutions and organizations from local communities for the realization of scientific events** - selection of topics for scientific events, determination of the manner for selection of the participants, methods of presentations at scientific events, proposing the list of institutions and organizations that will participate in scientific events.

2. **Preparing students to perform experiments, demonstrations, presentations at scientific events** - the implementation of preparatory workshops in partner institutions (Pictures 1 and 2)

Pictures 1 and 2. Preparatory workshops for students and partner institutions

3. **The realization of scientific events** - The Night of the Researchers in Bor and Zaječar, the Science Festival in Bor, Zaječar, Negotin and Knjaževac, where students are the main performers and promoters of science (picture 3). Each year, festivals are complemented with additional contents: a scientific theater "SCINEMASCIENCIA",

CPS`s program "Planetarium", etc. Through interactive contents and scientific quizzes the active participation of visitors in scientific activities is ensured (pictures 4 and 5).

Pictures 3-5. Scientific Festivals – students as a science promoters and visitors as active participants

4. Realization of scientific exhibitions in Bor, Zaječar, Negotin and Knjaževac (pictures 6-8)

Pictures 6-8. Scientific exhibition "Secret world of metals and minerals" at Museum of Mining and Metallurgy in Bor

5. Media campaign – project activities are followed and reported by all media in East Serbia, as well as through internet portals, networks and sites.

6. Project monitoring, evaluation and reporting - monitoring and evaluation activities were done by interviewing participants and visitors, and at the meetings of the project team. Based on the evaluation of the participants and visitors program activities were estimated to be very successful. On the base of comments and suggestions derived from the questionnaires project is being upgraded each year. The comparative analysis of festivals from 2013-2016. showed that the best rated aspect of festival was the *development of cooperative relations between the stakeholders*. Each year the number of participants in project, as well as individuals and institutions, is enlarging (Figure 1), so as the number of experiments, demonstrations and presentations (Figure 2). Project activities have spreaded from Bor to Zaječar and Negotin, and the cooperation with educational, scientific, cultural institutions, CSOs and businesses in these local communities has been established.

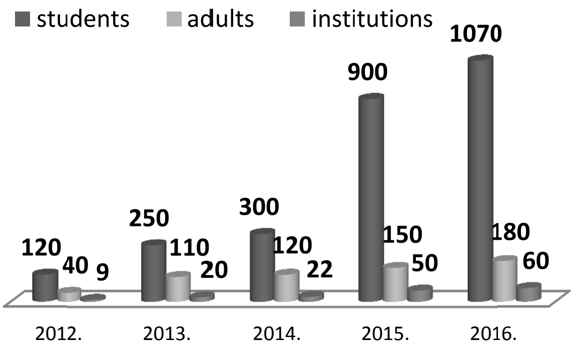

Figure 1. Change in the number of participants on scientific manifestations from 2012 to 2016.

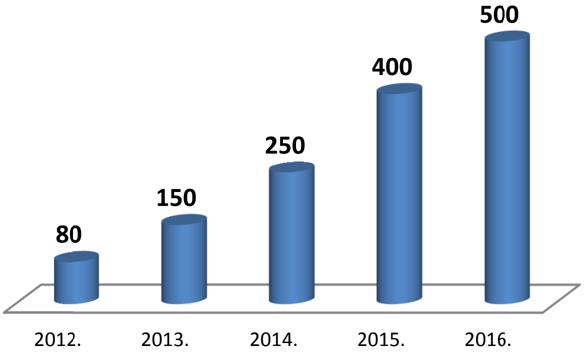

Figure 2. Change in the number of experiments, demonstrations and presentations on scientific manifestations from 2012 to 2016.

CONCLUSION

The complexity of the project objectives has resulted in the multiplicity of the project results, starting from the development of specific forms of education in the science popularization that allowed the improvement of students and teachers skills and competencies, increased the student`s level of knowledge and motivation for learning, developed cooperation between educational institutions and other institutions in local communities and beyond. Besides, through these programs talented students are given the special support in education, science, skills of practicing science have been combined, different types and departments of high schools and universities have been promoted, the use of existing or created teaching materials and peer learning has been promoted. A motivation of educational and other institutions (especially the teaching staff and students) for the continual improvement of science promotion through Scientific caravan TNT in the future has been increased. The plan is to expand the activities to other interested schools and municipalities in Eastern Serbia, and to establish international cooperation in the realization of the Science Festival.

REFERENCES

1. ****, 2012., Srategy for development of Education in Serbia by 2020. [in Serbian], URL: http://www.srbija.gov.rs/extfile/sr/179119/strategija_obrazovanje026_cyr.zip , Beograd
2. ****, 2016., Strategy of Scientific and Technological Development of the Republic of Serbia from 2016-2020. – Research for the Innovation [in Serbian],URL:http://www.srbija.gov.rs/extfile /sr/260093/ strategija_naucno-tehnoloski_razvoj205_cyr.zip , Belgrade
3. ****, 2015., National Strategy for Youth in Serbia for period 2015 – 2025. [in Serbian], URL: http://www.srbija.gov.rs/extfile/sr/232115/nacionalna_strategija_za_mlade0101_cyr.zip, Belgrade
4. Project reports on Scientific caravan "Timok Scientific Tornado – TNT" 2012. - 2016. , arhives of Association of Young researchers of Bor, Bor

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LEGAL AND PLANNING FRAMEWORK FOR NATURE PROTECTION - COMPARATIVE ANALYSIS OF AUSTRIA AND THE REPUBLIC OF SERBIA

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ABSTRACT

The topic of the study is specificity of the system of protection of natural parks in Austria and the Republic of Serbia. Similarities and differences of the system in analyzed countries are shown through the analysis of planning documents, legal and other legal regulations referring to nature protection, with special emphasis on problems of protection of areas of natural parks. The aim is to indicate to the possibilities of improvement and future direction of development of the system of protection of national parks in Serbia on the basis of examples of good practice of EU member countries.

Key words: Legal and planning framework, Nature protection, National park, Austria, Serbia.

INTRODUCTION

Human activities have influenced environmental changes, so now there is a common opinion about environment adapted to human necessities. Original intact landscapes are truly rare which is why ecologically prosperous countries invest significant efforts to preserve actual state of national landscape, both the intact and partly modified. This is exactly what numerous international organizations have claimed as one of the instruments for nature and environmental protection. A good representative of this approach is Austria, as an example of good management and protection of diverse spatial elements, whose experience can be applied to similar cases in Serbia.

Austria is a State Federation of nine federal units that are divided on urban and rural districts. The planning system and the environmental protection framework are based on the principal Austrian law “Grundegesetz” which is a pendant of a constitution. As such, it is a very important federal state, were the states (Länder) have a high degree of autonomy. The coordination between these several country parts is in the hands of the institutions on the national level.

Austria has a huge natural heritage, consisting inter alia of: 6 national parks (Neusiedler See – Seewinkel, Thayatal, Hohe Tauern, Kalkalpen, Donau-Auen and Gesäuse), 60 special nature reserves and nature parks, around 35 “hot spots” for bird watching and around 20 protected areas in the area of the Alps. These National parks are ecologically the most valuable parts of the federal territory including a large scale of natural and anthropogenic contents and 3% of the national territory (2.350 km^2). On this basis a few cross-border cooperation projects have been conducted with Hungary and Czech Republic (for Neusiedler See – Seewinkel and Thayatal National parks). All in all, these National parks are characterized by an extraordinary natural heritage, biodiversity, hydrographical, geomorphological and geological objects, phenomena and processes, requiring a particular regime of planning, arrangement and protection [3], [7], [9].

On the other side, on the basis of the institutional nature protection measures implemented for more than six decades, protected areas in Serbia amounts to 5753.1 km^2, or 6.51% of Serbia's territory, where there is a 461 protected areas: 5 national parks (National parks in Serbia are: Fruška gora, Đerdap, Tara, Kopaonik and Šar-planina), 17 nature parks, 20 areas with specific features, 68 nature reserves, 3 protected habitats, 310 nature monuments and 38 areas of cultural and historical significance [15].

In Serbia protected areas, depending on the value and importance, fall into three categories. Protected areas of great importance are the first category, which has international and national importance, and the national government declares them as such. The second category of protected areas are the ones of great importance to the provincial or regional level, which are proclaimed as such by the national government or a provincial body. The protected areas of local importance designated by the competent authority of local governments, constitute the third category of protected areas. When it comes to protected areas, National parks belong to the first category and are of the utmost importance for Serbia [15].

LEGAL FRAMEWORK

Austria

In this country nature protection (Naturschutz) is arranged by the complex system of laws and regulations that are in accordance with the EU directives. These laws are brought on the Länder level, meaning Länders are responsible for this legal segment. It is important to underline that all laws are mutually coordinated and that the legal base of all the federal states is similar – there are basic principles of nature protection which are adjustable to regional and state specificities. The Ministry of agriculture, forestry, environment and water management (Bundesministerium für Land-und Forstwirtschaft, Umwelt und Wasserwirtschaft) has the key role and an institutional responsibility in the area of nature protection. There are also some authorities under the auspices of the Ministry that have a particular role on the topic of nature protection - the Environmental Protection Agency of Austria (Österreichische Agentur für Umweltschutz) and several agencies and offices on the state level (Naturschutzfachstellen and Naturschutzabteilungen). The indicated institutions carry out professional tasks in terms of nature and landscape protection, identify problems, define protected areas of protected natural goods, but they also provide cooperation with the broader public involved. The primary legal acts are: The Law on Environmental Protection (Umweltschutzgesetz), The Nature Protection Law (Naturschutzgesetz), The Law on National Parks (Nationalparkgesetz), The Law on Spatial Planning (Raumordnungsgesetz), as well as numerous other laws and bylaws that regulate protection of plant and animal species, wild animals and hunting, protection of water, air and soil, waste management etc. [1], [9].

The Nature Protection Law, which is compliant to the international agreements and conventions, is the one that protects and promotes diversity and unity, that defines educative, scientific, cultural, biological and recreational values of landscapes and that adapts economic and social development to the natural resources. It establishes basic principles of nature protection. It includes a classification of protected natural goods, declares measures of protection and monitoring, defines jurisdiction of state authorities, penalties and fees and prescribes participation and free access to and exchange of information as obligatory. In addition this law also defines national parks as: natural ecosystems of special scientific or biological national or international significance that excel original natural and historical elements. Nature protection is set up on a permanent basis as a top priority of state and local authorities [1], [3], [7], [9].

The Law on National Parks – by the analysis of national laws a complex conclusion has been drawn: the Austrian National parks have impressive and rich landscapes that abound in beauty and originality of biodiversity. In order to provide nature protection and reduce human influence, the laws rely on IUCN (International Union for Conservation of Nature and National Resources) guidelines. This law determines land use within the National parks, primarily for education and recreation, science and researches. National parks represent intact or slightly changed landscapes, representative habitats of flora and fauna as well as cultural landscapes and historical objects as important elements of a protected area. The law specifies what are the prohibited activities and the National park authorities, bodies that will be responsible for control and monitoring and penalties for violation of its provisions. It claims the need of bringing a Declaration of the National park (Nationalparkerklärung) as an instrument that will help local authorities and communities to manage together protected areas and to dispose of them in an efficient and responsible manner. The state government has a duty to bring a National Park Management Plan (Managementpläne), apart from the Declaration, in order to define different areas of protection and the limits of the natural area, but also to regulate which activities are welcome within National parks and which ones are not. There is the three-stage protection regime (three zones of protection should be determined) in the area of the National park according to the laws and bylaws [1], [2], [5], [6].

The Law on Spatial Planning coordinates spatial development and the economic, social and cultural needs of a certain community that inhabits a particular area, for the sake of public interest and environmental protection, defines the mode of spatial and land use planning and the cases when construction is allowed or those when it is prohibited, like in the case of protected goods. Plans and programs are here classified into three categories: Development plan for the state, Program of development of the region and the Sector development plan (Landesraumordnungsplan and Raumordnungsprogramm). Local authorities bring and implement their local plans (Flächenwidmungsplan) in accordance with the plans of the higher order. As regards the environment and nature this law considers both their preservation and their planned and sustainable use in order to make the rest of it sufficient and of an adequate quality. The main issues are: protection of soil, flora, fauna, natural and cultural heritage, urban and rural landscapes [1], [4].

Republic of Serbia

Field of nature protection in Serbia is normatively regulated by The Law on Environmental Protection, Nature Protection Law and other laws and regulations that are directly or indirectly related to the nature and natural values. When it comes to national parks, especially important laws are The Law on National Parks and The Law on Planning and Construction. In addition to law enforcement, where the adoption of The Nature Protection Law which regulates the protection and conservation of nature, biological, geological and landscape diversity was of extreme importance, for the normative regulation in this area there are many bylaws which are also significant. Harmonization of legislation in the field of environmental protection and nature protection, with the EU, which is underway, European and international standards are taken into consideration and are implemented. Also, improvement and harmonization of nature conservation contributes to the implementation of the provisions and principles of international conventions of which the Republic of Serbia is a signatory [13], [14], [15]. Ministry of Agriculture and Environmental Protection of the Republic of Serbia is the central institution for the public administration tasks which are related to the system of protection and management of protected areas. Under existing law, the part of the competencies in the field of environmental protection is decentralized to the provincial level. Local governments, through the Secretariat for Environmental Protection, have responsibilities that are related to spatial planning, environmental protection and municipal services. Environmental Protection Agency is the body of the Ministry. This Agency performs state administration related to the development, coordination and management of the national information system for environmental protection; as well as cooperation with the European Environmental Agency (EEA) and the European environment Information and Observation Network (EIONET). In addition to the Ministry and the Agency on the basis of the Nature Protection Law competencies in the field of protection and improvement of the natural heritage of the Republic of Serbia and Autonomous Province of Vojvodina have been entrusted with the public professional institutions which are the Institute for Nature Conservation of Serbia and Provincial Institute for Nature Protection.

Law on National Parks regulates the goals, values, size, boundaries and regimes of protection, management and sustainable use of all five national parks in Serbia. By this Law, the protection and sustainable use of the national park is carried out according to the National Park Management Plan for the period of ten years and other acts adopted on the basis of laws, regulating the protection of nature [10]. The management plan includes measures, prohibitions and limitations of works and activities in accordance with prescribed protection regimes. Management plans, are adopted by Public companies - managers of national parks as an obligation. Also, managers are required to ensure internal order and safeguarding of protected areas in accordance with The Rules of Order and the Guardian service, which are made with the consent of the competent authority [10], [15]. Within the National park are determined protection regimes of first, second and third level (closer regulated by The Regulation on the Protection regimes), in which are applied prohibitions and restrictions on work and activities identified in the Management Plan and regulations governing the protection of nature. These activities, as defined in the Management Plan, and harmonized with the Spatial Plan for Special Purpose Areas, forbid the construction of buildings that are in contradiction with the present plan [10], [15].

PLANNING FRAMEWORK

Austria

The process of spatial planning in Austria (Raumordnung and Raumplanung) is an arranged and complex system of plans on the federal, state, town or municipality level. States are responsible for Regional plans, both for their drawing and implementation. These regional plans are very significant because they are crucial for setting principles of systemic and sustainable organization of space, with the aim of rational land use, special areas and environmental protection. Towns and municipalities are competent for land use planning and nature protection on local levels, by local regulations and plans. So, land use planning is of great importance for nature and space protection in Austria, being an interactive process consisted of dialogs between all the interested actors in order to define a sustainable form of land use [3], [4]. Is important here to mention LISA (Land Information System Austria) which has the purpose of collecting and present actual and detailed geospatial data for the purposes of state authorities and the private sector about development level and actual state of soil and land use in Austria. All these planning levels – the federal, state and local are connected by ÖROK (Österreichischen Raumordnungskonferenz). ÖROK is a complex organization which deals with the application of EU regional policies on the federal level and also with diverse analysis, researches and statistics. It is a managing authority for EU programs [9].

The soil and ecosystems within the Austrian National parks need a special regime of planning and management to be sustainable. Planning documents are, apart from laws and other regulations, another instrument for protection and development of nature goods. Among them, Regional plans as planning documents of the highest level, determine basic, long-term objectives in the field of nature protection, allocate and set out important protected areas within the planning area, lay down general guidelines for planning and management and measures to protect natural resources, whereby the emphasis is on national parks as natural areas of greatest ecological value (if existing in the area to be treated). Local plans that refer to municipalities (Flächenwidmungsplan) or Land use plans must adopt basic principles and guidelines from the planning documents of the higher level and should implement and respect them. Local self-government carries out a zoning process with the help of these plans and sets aside areas for different purposes, separating residential zones, work zones, green areas, etc. [1], [4], [8].

The most important document in the field of protection and management of National parks is the National Park Management Plan (Nationalpark Managementpläne) [5], [6]. This Management Plan together with the Declaration of a National Park represents an instrument for sustainable development of natural goods. The Management Plan is a long-term document that is brought usually for a 10 years period. A company that manage a National park brings this plan in order to precisely define the boundaries of the treated protected area, disposes the protected zones within them and designates what activities can be placed in that area. The drafting of a Management Plan is based on the real situation, so its implementation could be complete. Management Plans in Austria have the role in achieving the objectives, which means they aren`t only "wish lists". This implies that the majority of those objectives is realized in the time horizon of the plan, making a significant difference comparing to the Republic of Serbia. First, the Management Plan defines land use within the area of a National park and emphasizes what are the most important allowed activities: agriculture, forestry, hunting and fishing, tourism and other economic activities that are represented here, spatial development and others. This is followed by an overview of the state of the environment and an identification of the most valuable natural parts, representative specimens of flora and fauna and their habitats and if there are, those spatial entities that are in a "worse condition". Finally, it defines the scenarios for future development, lays down measures to protect the environment, regulates the system of monitoring and evaluates priority activities [5], [6].

Republic of Serbia

The planning framework for the regulation and protection of areas of the national parks in Serbia is based on spatial planning documents. The Law on Planning and Construction prescribes four types of spatial plans which are to some extent related and treat protected areas of national parks: Spatial Plan of the Republic of Serbia, the Regional Spatial Plan, the Municipal Spatial Plan and Spatial Plan for Special Purpose Areas [11]. Spatial Plan of the Republic of Serbia (SPRS) passed for the territory of the Republic, is the basic planning document of spatial planning and development in Serbia, and all other documents (plans) must comply with it. This plan, which have strategic development and general regulatory function, defines all the protected areas of international, national and regional importance in Serbia. In the context of ecological connectivity, order and sustainability, national parks have a special place and were recognized as areas protected, maintained and with adequately presented natural and cultural values. As for the elements of the environment, national parks are seen as areas of high-quality environment which require planning solutions to keep the existing state of its quality and protect valuable and preserved natural ecosystems [11], [12].

Regional Spatial Plan (RSP) is made for larger spatial entities with administrative, functional, geographic or statistical character, aimed towards common objectives and projects of regional development. The RSP is a planning document with respect to specific needs arising from regional particularities, and elaborates the objectives of physical planning and determines rational use of space, in line with neighbouring regions and municipalities, while respecting the strategic solutions and recommendations of the SPRS. In this context, protected areas are treated when a part or the entire area of the national park is in the scope of the RSP [12].

Municipal Spatial Plan shall be adopted for the municipal territory and determines guidelines for the development, land use and conditions for sustainable and balanced development within its territory. Similar to RSP, when the territory of the municipality is part of the national park or a complete municipal territory falls within the scope of the national park, the plan must comply with all orders and directions given higher level plans (SPRS and RSP) [12].

Spatial Plan for Special Purpose Areas (SPSPA) shall be adopted for areas that require special regime of organization, development, use and protection of space, projects of importance for the Republic of Serbia or for areas designated by the SPRS [9]. This applies to national parks as areas with natural values, as well as the areas with the possibility of using tourism potential, which makes it the most important planning document when it comes to national parks and protected areas. SPSPA is adopted by the Government of the Republic of Serbia, at the proposal of the ministry responsible for regional planning, while for areas located entirely within the territory of the autonomous province brings the Government of the Autonomous Province. SPSPA for the area of the National Park contains first, second and third level of regimes of protection, which are prescribed by the Law on National Parks [10], [11].

Urban development plans defined by the Law on Planning and Construction: General Urban Plan, Plan of General Regulation and Plan of Detailed Regulation, when made for the part of the National Park (settlements, resorts, undeveloped areas etc.) must be harmonized with the SPSPA and respect the established regimes of protection. Urban development plans shall be adopted with prior approval of the Ministry of Agriculture and Environmental Protection and the Ministry which is responsible for urban and spatial planning in Serbia. Until the adoption of urban development plans, the terms of the regulation, use and protection of individual locations are also determined after receiving approval from the competent Ministry [10], [11].

CONCLUSION

The analysis of the planning and legal framework of Austria and the Republic of Serbia led to the conclusion that the planning systems and legislative provisions of the two countries are based on principles of sustainable development. The Laws, according to the character and content, are very similar, which is the result of harmonization of national legislation with international conventions and EU directives.

The biggest difference between the observed countries is the way of law enforcement and implementation of planning documents. Austria as a strong and regulated federal state has developed the local level that is able to actively participate in the realization of the set goals. On the other hand, local governments in Serbia, weakened by the negative trends that are deeply rooted and difficult to overcome, have no other solution but to seek and rely on help of the state and its intervention in space. Also, a significant difference is the fact that the implementation of planning documents is the weakest link in spatial and urban planning in Serbia. This is the result of expressed generalization of planning solutions. On the other hand, in Austria, national and local level are very responsible in implementing the decisions which are defined in planning documents. Planning solutions are very clearly and specifically defined, and sustainable land use is one of the main tasks of the community.

Other previously mentioned obvious difference is the implementation of the law. The laws are very similar, with the big difference in the degree of compliance with legal provisions. Structure and harmonization of Austria as a complex state is based on the strict respect of all types of legal acts which are adopted, while in Serbia, a common practice is to find "legal loopholes" and "Stretching the Rules" or contempt of legal acts, which can be interpreted as the result of less rigorous punitive measures. The dominant cause of this is the low level of political responsibility, ignoring the opinions and suggestions of experts, symbolic participation and lack of civic discipline. Also, Serbia has gone through a very difficult transition period that left deep traces on the functioning of the country in all segments of the community. For this country is of great importance to collect positive experiences of developed European countries, such as Austria, which can be used as a model for future sustainable and more effective development in the field of nature protection as well as in other areas important for a legally stable and well organized country.

REFERENCES

1. Das Rechtsinformationssystem des Bundes (RIS) [The Legal Information System of the Republic of Austria], https://www.ris.bka.gv.at/Land/.
2. Gesetz über die Errichtung und den Betrieb des Nationalparks "Oö. Kalkalpen" (Oö. Nationalparkgesetz - Oö. NPG) [Law on National Parks in Upper Austria] LGBl.Nr. 90/2013.
3. Gesetz über den Schutz und die Pflege der Natur und Landschaft im Burgenland [Law on the Protection and Care of Nature and Landscape in Burgenland], NG 1990, LGBl. Nr. 20/2016.
4. Gesetz über die Raumordnung im Land Oberösterreich [Law on Spatial Planning in Upper Austria] (Oö. Raumordnungsgesetz 1994 - Oö. ROG 1994), LGBl.Nr. 69/2015.
5. Managementplan Nationalpark Donau-Auen 2009 – 2018. [Management Plan of National Park Donau-Auen]. (2009). Orth an der Donau: Nationalpark Donau-Auen GmbH, Schloss Orth.
6. Managementplan Nationalpark Thayatal 2010 – 2020. [Management Plan of National Park Thayatal]. (2010). Hardegg: Nationalpark Thayatal GmbH.
7. NÖ Naturschutzgesetz 2000 [Nature Protection Law in Upper Austria], (NÖ NSchG 2000), LGBl. Nr. 38/2016.
8. ÖROK – Österreichische Raumordnungskonferenz [The Austrian Conference on Spatial Planning], http://www.oerok.gv.at/.
9. Umweltbundesmt [Austrian Environmental Protection Agency], http://www.umweltbundesamt.at/en/.
10. Zakon o nacionalnim parkovima [Law on National Parks] ("Službeni glasnik Republike Srbije", br. 84/2015).
11. Zakon o planiranju i izgradnji [The Law on Planning and Construction] ("Sl. glasnik RS", br. 72/2009, 81/2009 - ispr., 64/2010 - odluka US, 24/2011,

121/2012, 42/2013 - odluka US, 50/2013 - odluka US, 98/2013 - odluka US, 132/2014 i 145/2014)

12. Zakon o Prostornom planu Republike Srbije od 2010. do 2020. godine [Law on Spatial Plan of the Republic of Serbia from 2010 to 2020] ("Službeni glasnik Republike Srbije", br. 88/2010).
13. Zakon o zaštiti prirode [Nature Protection Law] ("Službeni glasnik RS", br. 36/2009, 88/2010, 91/2010 – ispr. i 14/2016).
14. Zakon o zaštiti životne sredine [The Law on Environmental Protection] ("Službeni glasnik Republike Srbije", br. 135/2004, 36/2009– dr. zakon, 72/2009, 43/2011 – odluka US i 14/2016).
15. Zavod za zaštitu prirode Srbije [Institute for Nature Conservation of Serbia], http://www.zzps.rs/novo/index.php?jezik=en&strana=naslovna.

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POSSIBILITIES OF IMPROVEMENTS IN MANAGING SUSTAINABLE DEVELOPMENT OF WATER TRANSPORT ON THE DANUBE

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ABSTRACT

In order to manage a sustainable development of water transport on the Danube, it is necessary to analyze the current state, identify possibilities and define actions that will improve further sustainable water transport. This paper provides a brief overview on the possibilities of improving water transport on the Danube in Serbia in a sustainable way, so as to significantly reduce the impact on the environment and the water quality of the river.

Key words: improvement, sustainable development, the Danube.

INTRODUCTION

The Danube River is the most important waterway of Europe. About 300 tributaries flows into the Danube where 180 of them are, according to hydrological significance, very important; 120 are medium rivers, while 34 of it are rivers navigable for ships. In general, length of the navigable tributaries of the Danube is about 1,928 km. Hydrological system "Danube-Tisa-Danube" (DTD) waterway has a length of 664 km. When you add the total navigable length of the Danube, which is 2,580 km starting from Ulm to the Black Sea, it results in 5,172 km of an overall length of navigational waterways in the Danube basin. So Danube, by relevance in the global inland waterway traffic, occupies sixth place after the Mississippi, the Rhine, the Ohio, the Yangtze River and the Volga. However, according to its significance to Europe, it is just around the Rhine and the Volga (Figure 1).

Development planning of certain traffic arteries is an opportunity for economic development [1]. However, the importance of the transport aspects of the Danube has not been always seriously considered. Primarily, due to political reasons, before the mid-20th century, the river was not representing a viable bond of Transport and Communications. After the Second World War, however, the effective internationalization of the river, making of extensive projects for the improvement of navigation, construction of dams and hydropower plants, as well as significantly faster economic development of the Danube basin as a whole, has contributed greatly to the

Danube in becoming the center of the European axis and regional interconnections [2]. It is therefore significant that transport corridor network, which represents a long-term strategic option of the European Union, includes Serbia.

Figure 1. The Danube Basin along the entire length from the source to the mouth

The main Serbian links via the Danube are achieved upstream with Croatia, Hungary, Slovakia, Austria and Germany, and downstream with Romania, Bulgaria, Moldova and Ukraine. From the Hungarian border to Belgrade, the Danube runs almost parallel to the route of European highway and railway line, so the area makes it extremely valuable and important from the economic and every other point. This was confirmed by the fact that in the period from 2001 to 2009, the area along the Danube and in its coastal areas was invested by foreign investors with more than two-thirds of all foreign investments in Serbia [3].

The revival of activities at the corridors that pass through Serbia (Corridors VII and X), brought back the high possibility of economic and sustainable development to not only the citizens of Serbia, but also to the entire European continent [1]. Pan-European "Corridor VII" is the Danube River itself, which is one of the five transport corridors that are located in the region of Southeast Europe. From a total of ten European corridors, only the "Corridor VII" is a waterway, while the other nine are the land routes. That in itself speaks about multiple traffic significance of the Danube, which has always been at the center of international events. "Corridor VII" is an important strategic bond with Europe and Euro-Asia which should encourage the development of trade, tourism and services in Serbia.

AN OVERVIEW OF WATER TRANSPORT ON THE DANUBE IN SERBIA

Nowadays, there are around 5,200 cargo ships navigating on the Danube. Only 24 docks achieve turnover that exceeds 1 mil. tonnes, including the Port of Belgrade (with 1.5 mil. tonnes) and Smederevo (1.2 mil. tonnes) in Serbia. Nevertheless, the state of the river fleet in Serbia is poor due to unfavorable age structure and technological obsolescence. Since 1995 not a single ship has been built. For certain types of vessels, only about 6% of just two types of vessels have been built in the last 20 years.

Important multipurpose hydraulic system, whose main function is irrigation and drainage, but also with the existence of the actual conditions for the navigation, is certainly Hydro-system DTD (Danube-Tisa-Danube). It consists of 12 water canals of two regions (Bačka and Banat), with the total navigable length of 600 kilometers, which are classified into four categories of waterways. It is one of the largest navigable canal networks in Europe, which in addition includes waterways and channeled rivers Begej and the Tamiš. There are 16 ship locks built on the DTD canals, 12 of which can accommodate vessels up to 1,000 tonnes, and four boats up to 500 tonnes. Some of the reasons for the relatively low usage of the canal for navigation are insufficient width of the channel, the lack of marking and navigation signs, underwater and coastal vegetation, etc. Domestic vessels mainly transport goods in one direction and short-range, where the fees are being charged for the use of canal, while the passage of foreign ships requires permission of the ministry in charge [4].

Thanks to the development of economic relations between the Danubian countries, free navigation and improved conditions for navigation, freight transport on the Danube, from the 50s to the late 80s of the twentieth century, has increased almost tenfold and reached nearly 91.8 million tonnes. Loading and unloading at the Danube ports has increased and reached more than 150 million tonnes. Companies in the industry of inland waterways Serbia disposed at the end of 2008 with about 400 vessels, of the available capacity of approximately 403,833 tonnes and a total output of 60,000 kW. Over 77% are vessels for the transport of dry cargo, while the rest are vessels for the transport of liquid cargo [5].

The main challenges of the implementation and development of the internal water transport based on cargo vessels are concerning the difficulties in constructing adequate, sustainable infrastructure, but it is also necessary to fulfill the requirements concerning the protection of the environment and human health [6]. Transport on inland waterways can have a very negative impact on the environment, due to non-compliance with standards in the field of environmental protection. The pollution caused by spills, discharge and disposal of waste from vessels could then cause pollution of drinking water, a break in the usage of water for industrial purposes, as well as to reduce the quantity of available water for irrigation.

Generally, performance of water traffic causes waste pollution from large ships. In particular, the lack of fitting port facilities with appropriate equipment for the collection, treatment and disposal of waste materials and oily waste water from the ships along with other factors are important threat to water quality of the Danube. Likewise, the cross-border transit of water pollution of the Danube and its tributaries entering Serbia lead to distortions of the environment and affect the water quality of the Danube River [7]. Amounts of solid waste discharges from ships at ports on Danube for the year of 2012 are shown in table 1. It can be concluded that during the observed time period, the largest waste release was in Novi Sad port, which should concern the authorities to urgently take necessary actions about it. Also, in comparing these amounts of solid waste discharges with data from the previous years, Petrović [7] concluded that there is a certain tendency of waste product increase in Danube caused by water transport being carried out which will certainly have negative impact on the quality of water.

Table 1. Amounts of solid waste discharge from ships at ports on Danube River in 2012

Ports on Danube	**Amount of solid waste (tonnes per year)**
Bezdan	351
Apatin	25
Bačka palanka	27
N. Sad	1027
Beograd	558
Smederevo	89
Veliko Gradište	100

Improving traffic on inland Danube waterway would necessarily lead to an increase in the impact on the environment including a pollution of navigable watercourses in oil and derivatives and pollution from the vessels at the waterways. The solution lies in a better way of managing river vessels, thus reducing the pollution of watercourses and improving water quality at no extra cost, where better management requires a comprehensive approach in terms of integrated river basin management, in accordance with the Water Framework Directive of the EU [8].

TENDENCIES OF EFFICIENT MANAGEMENT OF WATER TRANSPORT ON THE DANUBE IN SERBIA AND ON TERRITORY OF THE EUROPEAN UNION

Water transport offers significant economic and environmental benefits, particularly in relation to road transport, but in spite of mild positive developments, it is still neglected in relation to other forms of transport.

About 70% of the total trade between the EU and the rest of the world has been performed through the ship's transport. Annually, the European port passes over two billion tonnes of different goods. However, there is no significant progress in changing the "modal split", simply because there are no good connections with inland waterways and rail, so that the bulk of goods goes by road transport. In other words, intermodal transport, in concrete terms, has not become an alternative to road transport yet. Maritime transport and inland waterway transport are the two basic components of intermodal transport, which would have to be alternative transport to saturated roads and railway infrastructures. This potential is almost unlimited (35,000 km of coastline and hundreds of sea and river ports) [9].

In order to activate these potentials, one of the possible solutions would be to build sea motorways and offer efficient, simplified services. For the development of pan-European networks for the transport of marine cargo, giving priority to the docks at the national level who have good relationships with internal networks, particularly on the Atlantic and the Mediterranean coast is essential, in order to form authentic logistics chain.

Strategy involves the use of European regulations and guidance documents for the development of inland waterway transport infrastructure in accordance with the environmental requirements. In this regard, as especially important, the application of the Water Framework Directive [8], the Directive on strategic environmental impact assessment [10] and the Directive on the impact on the environment [11] should be noted. Also, the importance of the process of arranging the three river commissions, and the Danube Commission (DC), the International Sava River Basin Commission (ISRBS) and the Commission for the Protection of the Danube River (ICPDR), which together in "Joint Statement on Guidelines for the Development of Inland Navigation and Environmental Protection in the Danube river basin" [12] in 2007, emphasized the need for integrated development planning process of waterways. One of the instruments for its implementation is "Instructions for achieving good practice in sustainable planning of navigation" [13] which represents an integrated approach to planning the way of the river infrastructure, thus predicts the development of waterways in the basin of the Danube River in accordance with European standards and environmental requirements.

As for solving the problem of waste discharges from ships in Serbia, there is Regulation 1013/2006 on transboundary movement of waste [14] that regulates the supervision and control of transboundary movements of waste. This regulation in European legislation transposed the provisions of the international Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their release defining the norms of procedure and criteria for the management of waste in compliance with the protection and improvement of the environment. Countries applying this Regulation shall determine the appropriate authorized organizations for waste transportation.

One of the greatest treasures of the EU is just a very extensive network of rivers and canals linking the basins of the Atlantic and the North Sea as well as the Black Sea through the Danube and the R-M-D. Annual range of transport on the Danube is about 425 million tonnes of goods. In addition to the regional system, a series of European countries is linked to river and canal systems with the northwest and North Sea harbors. In relation to the available infrastructure and means of transport, this part of the transport system of the EU (and beyond) is not being exploited enough, as a direct result of inadequate internal policies relating to investment, where a priority is given to other modes of transport, without maintaining the waterway network nor eliminating narrow throats. The methodology should include calculations of disproportionate costs, assessment methods for adverse effects and better environmental options. The use of green infrastructure or natural water retention measures, for example, that provide a range of environmental improvements in water quality, flood protection, habitat conservation etc., along with plenty of social and economic benefits, can be in many cases more cost effective than grey infrastructure.

CONCLUSION

Since river transport significantly affects the environment and increases efficiency, its potential must be sustainably exploited. The Danube is an important trans-European waterway. However, it is used way below its full capacity, which is why there is a particular need for more modality, better interconnection with other river basins by modernizing and extending infrastructure in transport nodes.

It is generally acknowledged that the lack of infrastructure for the protection of the environment, poor environmental management practices, as well as poor enforcement of laws and regulations in the field of environmental protection, are an obstacle for sustainable socio-economic development of the country. The Danube region is an international hydrological basin and ecological corridor, which necessarily requires a regional approach to nature conservation, spatial planning and water management.

Large floods, droughts and industrial pollutions are happening far too often. Prevention, preparedness and effective reaction require a high degree of cooperation between our country and the exchange of information with other countries in the Danube region. These challenges are best approached together, identifying priorities, agreeing and implementing actions. Specialists for development and protection of the environment must find innovative solutions, resolving together the most difficult issues for the benefit of the entire Danube region.

REFERENCES

1. Stojić-Karanović E. (2002). Otvorena pitanja i perspektive saradnje podunavskih zemalja, Saradnja podunavskih zemalja MP 3, 221-252.
2. Weigend G.G. (1975). The Danube River: an emerging regional bond. Geoforum, (6) (2), 151-161.
3. ICPDR (2005). WFD Roof Report 2004 Document IC/084, 2005. Available at: http://www.icpdr.org/icpdr-pages/tnmn.htm
4. Strategija (2010). Strategija Evropske Unije za Dunavski region, Evropska Komisija, Brisel, COM (2010) 715/4. Available at: http://www.dunavskastrategija.rs
5. RZS (2009). Republički zavod za statistiku, Bilten „Saobraćaj, skladištenje i veze za 2009".
6. Horváth N. (2011). From development to sustainability? The EU Strategy for the Danube Region, 8th DRC (Danube Rectors' Conference) Summer School on Regional Co-operation, Proceedings, 85-96.
7. Petrović, Lj. (2015). Spatial development analysis of the Danube region in Serbia in the function of sustainable development. Bulletin of the Serbian Geographical Society 95 (4), 141-158.
8. EU Water Framework Directive. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 Establishing a framework for Community

action in the field of water policy (http://ec.europa.eu/environment/water/water-framework/index_en.htm).

9. Smernice za poslovanje sa Evropskom unijom (2006). Saobraćaj, Fond za evropske integracije, Beograd, 2006.
10. Directive 2001/42/EC of the European Parliament and of the Council of 27 June 2001 on the assessment of the effects of certain plans and programmes on the environment. OJ L 197, 21.7.2001, p. 30–37
11. Directive 2011/92/EU of the European Parliament and of the Council of 13 December 2011 on the assessment of the effects of certain public and private projects on the environment Text with EEA relevance. OJ L 26, 28.1.2012, p. 1–21
12. Joint Statement on Guiding Principles for the Development of Inland Navigation and Environmental Protection in the Danube River Basin.
13. Manual on Good Practices in Sustainable Waterway Planning. SWP 5.3 Infrastructure – Support inderdisciplinary dialogue on environmentally sustainable waterway development, ICPDR, Platina, July 2010. Available at: https://www.icpdr.org/main/sites/default/files/Platina_IWT%20Planning%20Manual.FINAL.Aug10.c.pdf
14. Regulation (EC) No 1013/2006 of the European Parliament and of the Council of 14 June 2006 on shipments of waste

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DEVELOPMENT OF UNDERGRADUATE VOCATIONAL PROGRAM IN THE FIELD OF WASTE MANAGEMENT

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ABSTRACT

Learning outcomes and competence-based education at any social level is of great importance. One of main aims of WaMPPP project (Waste management curricula developement through partnership with public and private sector) is to enhance education of current and future workforce in Serbia in the field of waste management (WM), through development of modern curricula and syllabi, based on real needs for a competent workforce in the WM sector. Towards obtaining this goal survey had been conducted within professionals in the WM field as well within organizations connected with WM sector. This paper presents some of obtained results of this survey.

Key words: qualifications, survey, waste management, education.

INTRODUCTION

The value of competence-based education at any social level is essentially an economic consideration [1]. Students have to shift their thinking away from a science - and subject-based approach, towards vocational study structures based on working life activities and functions [2]. Learning outcomes and competence-based vocational and professional education highlights the core principle of aligning competence needs with the societal standards, norms or expectations regarding task performance [3]. The shift from a basically subject-based model to a work and learning outcomes could increase the labour market relevance of education, in other words, the need for skilled labour force and for a common language between education and working life [2]. Before drawing any firm conclusions about which factors are important and how these interact in their context, evidence should exist out of quantitative (e.g. surveys) or qualitative (e.g. interviews) data and other relevant documents.

College of Vocational Studies Belgrade Polytechnic concluded survay within stakeholders with the aim to define important qualifications of graduated students, towards obtaining the vocational skills requirements of stakeholders directly or indirectly connected with waste managment practis. Some of organizations included in survey were SET Reciklaža, BiS Reciklažni centar, Victoria Group a.d., CRH Agregati a.d.

(Popovac) SUPERLAB, Hemofarm a.d., Milanović inženjering (Kragujevac), Jakob Becker d.o.o. (Ruma), and others.

RESULTS AND DISCUSSION

In the focus of survey were competencies of graduates of undergraduate vocational studies. Questionnaire (named : *Questionnaire on required competencies of graduate students)* had been formed, with incorporated expected qualifications of students after graduation, grouped in three specific fields of interest - *knowledge, skills* and *abilities and attitudes*. Respodents, local business and industry stakeholders, in the WM field as well within organizations connected with WM sector (35 of them) evaluated each given criteria with value between "1" - the least importance to "5" - the highest importance, according competencies that would be relevant and appropriate for an undergraduate degree, and expectations from students in workplace after graduation.

Expected qualifications in the field of *knowledge*

Qualifications in the *knowledge* field that were valued by stakeholders are given in Table 1. (each criteria were assigned with one value, from "1" - the least importance, to "5"- the highest importance).

Table 1. Qualifications in the *knowledge* field that were valued

Q1	Apply the principles of waste management
Q2	Knows the properties of different types of waste materials
Q3	Apply national and European legislation
Q4	Apply knowledge about waste management practices, such as collection, sorting, transport, treatment and disposal of waste
Q5	Collect and interpret data generated in the processes related to waste management
Q6	Proposed measures to improve waste management related procedures
Q7	Knows how to apply knowledge in a professional manner in the field of waste management

Fig.1 shows obtained results - expected qualifications in the *knowledge* field, after completing undergraduate vocational studies (Level of Studies: Undergraduate vocational studies; Length of study program: three years; ECTS: 180).

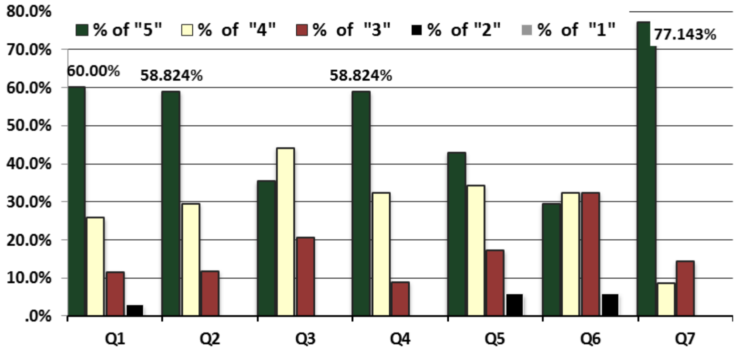

Figure 1. Expected qualifications in the *knowledge* field after completing undergraduate vocational studies

Based on the obtained results of the survey, graduates of undergraduate vocational studies in the field of waste management, should set as a priority Q7- Knows how to apply the knowledge in a professional manner in the field of waste management, as this quality is highly desirable by future stakeholders (77% of them circled value "5"). Highly valued qualifications in the knowledge field are : Q1-Apply the principles of waste management, Q2- Knows the properties of different types of waste materials, an Q4- Apply knowledge about waste management practices, such as collection, sorting, transport, treatment and disposal of waste (each with about 60% with maximum value "5"). Of less importance for stakeholders are Q3- Apply national and European legislation and Q6 - Proposed measures to improve waste management related procedures.

Expected qualifications in the field of *skills*

Qualifications in the *skills* field that were valued are given in Table 2.

Table 2. Qualifications in the *skills* field that were valued

Q8	Searches and uses professional literature
Q9	Informs superiors of the results of the work process
Q10	Verbal and written communication with the environment in native language and English
Q11	Take samples of waste
Q12	Experimentally determines the composition of waste and its energy value
Q13	Conducts monitoring of gases and wastewater, generated in waste management processes
Q14	Participates in multidisciplinary projects in the field of waste management

Fig.2 shows obtained results - expected qualifications in the *skills* field, after completing undergraduate vocational studies (Level of Studies: Undergraduate vocational studies; Length of study program: three years; ECTS: 180).

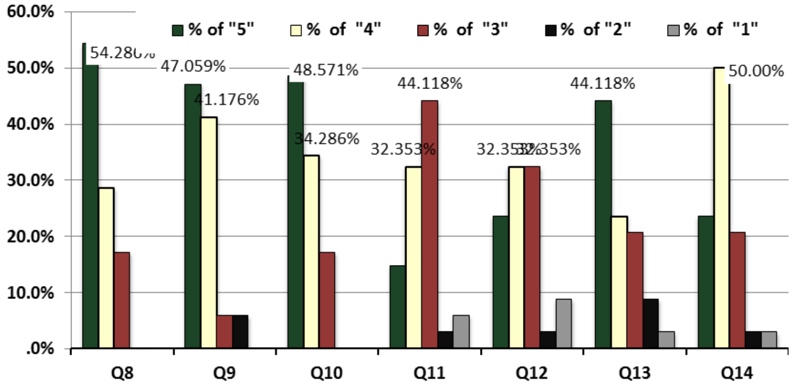

Figure 2. Expected qualifications in the *skills* field after completing undergraduate vocational studies

Qualifications Q8 - *Searches and uses professional literature*, Q9 -*Informs superiors of the results of the work process*, and Q10 -*Verbal and written communication with the environment in native language and English,* are highly rated, as more than 80% of respondents – entrepreneurs considered these as important skills. While Q12-*Experimentally determines the composition of waste and its energy value,* is not as important for stakeholders. This can be explained with difference between companies included in survey, but it can also be concluded that skills such as experimental determination of the composition and energy value of the waste, as well as sampling of waste (Q11), are not the priority for them, considering this level of education.

Expected qualifications in the field of *abilities and attitudes*

Qualifications in the *abilities and attitudes* field that were valued are given in Table 3.

Table 3. Qualifications in the *abilities and attitudes* field that were valued

Q15	Capability to continue studies
Q16	Analyzes the experimental data and evaluate their impact on the environment
Q17	Informs authorities about the possible harmful effects on the environment
Q18	Works independently
Q19	Works as a team member
Q20	Patience and adaptability

Fig.3 shows obtained results - expected qualifications in the *abilities and attitudes* field, after completing undergraduate vocational studies (Level of Studies: Undergraduate vocational studies; Length of study program: three years; ECTS: 180).

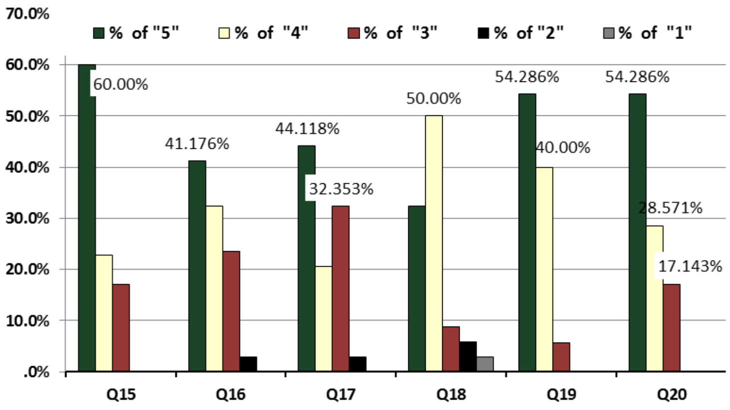

Figure 3. Expected qualifications in the *abilities and attitudes* field after completing undergraduate vocational studies

According Fig. 3, qualification under Q15 -*Capability to continue studies* choose 60 % of the surveyed entrepreneurs, they also choose Q19 - *Works as a team member* (94% given as sum of "5"and "4"), as well as for Q20- *Patience and adaptability*- 93%.

CONCLUSION

One of main aims of Erasmus+ project, WaMPPP (Waste management curricula development through partnership with public and private sector) is to enhance education of current and future workforce in Serbia in the field of waste management (WM), with one of specific goals - development of modern curricula and syllabi, based on real needs for a competent workforce in the WM sector. Conducted survey within professionals in the WM field as well among organizations connected with WM sector, represents a good basis for development of a new undergraduate vocational studies program, which will be in accordance with the needs of the stakeholders.

REFERENCES

1. Ryan, R.: How VET responds: A historical policy perspective, National Centre for Vocational Education Research, Adelaide, 2011.
2. Inspiring and strengthening the competence-based approach in all Vet in Finland – Support material for implementation, Guidelines for education providers, Finnish National Board of Education, 2015, ISBN 978-952-13-6050-3
3. Mulder, M: Competence-based Vocational and Professional Education - Bridging the Worlds of Work and Education, Technical and Vocational Education and Training: Issues, Concerns and Prospects, Volume 23, 2017, ISBN 978-3-319-41713-4

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ENVIRONMENTAL RESPONSIBILITY IN TRANSITIONAL ECONOMY

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ABSTRACT

In circumstances where the various and numerous external effects lead to the inefficient allocation of natural resources, the application corresponding economic instruments, such as various forms of sanctions, taxes, and grants permission, has a crucial importance. Changing the mode of production, change inputs, the introduction of a system for controlling pollution reduction are one way to achieve a reduction of environmental pollution. The negative consequences of human impact on the industry and the environment have been overcome in the development of transition economies so that they create the conditions of ecological crisis that is able to make the environment hostile to human life. Shift of negative human impact on the environment positively, is one of the main tasks for the further sustainable development of mankind.

Key words: ecology, sustainable development, environment, economic instruments.

INTRODUCTION

Among the many existential crises, with which humanity faces today, the ecological crisis is a special place. Protection and improvement of environment have become a global problem of modern society. The environment as an area of research and environmental responsibility at the beginning of XXI century, attracting the attention of scientists and practitioners of various sciences. Existing problems are imposed science and operations, emphasized the actuality and acuteness, all clearly leads to the conclusion that a healthy environment does too, that many elements in it vulnerable to the degree of self-regulation of certain assets is insignificant and that once disturbed ecological relationships almost nothing and can never be brought back to its original state.

Faced with problems of growth and its social consequences, transition countries are trying at all costs to open new areas for growth in new sectors, thereby damaging the very foundations of the system. Their main hope lies in new technologies as well as stimulating the vitality of the system, not in changing social attitudes. They are helped by the ecological critique that for the most part covers the consequences, rather than social causes in the system.

EXTERNAL FACTORS OF POLLUTION

Social reproduction requires suitable treatment of the natural environment. Creating a common policy, which respects the principles of economy growth and sustainable development, requires dynamic intersection of economic, social, ecological and institutional subsystems. In terms of sustainable development, the relationship between economy and ecology, emphasis is given on the basis of the perception of the environment as a source of resources for economic activity. Environmental movement so often meets grassroots supporters and activists of the "small" successes, but also equity holders of the warnings which way to invest capital so that everyone in the company were satisfied. This part of the ecological critique and holders of its functional fit into the system and should complement each other as well as its economic and social barometer[1].

Accelerated industrialization and exploitation of non-renewable resources with environmental pollution, water economy towards self-destruction and catastrophic wars for food, energy, space and water. Environmental pollution, primarily water and air, the phenomenon that economists call external effects. They are the result of imperfect operation of the market mechanism.

When a factory discharges chemicals into the nearby river, it thus increases the cost of water purification, enterprises located downstream. These are the negative external effects. In contrast, the positive external effects, the activities of persons who provide benefits to others.

In transition countries, the population is not sufficiently motivated to improve the quality of not only the environment, but also the factors of production. In market economies, the benefits of such positive actions are reflected in the market price of an asset or production factor. Problems negative external effects can often be overcome by defining property rights, because it allows the owner the right to control the exploitation of resources, and charge a fee for use. In certain cases, private markets cannot solve the problem of externalities without government interference. The optimal way to internalize externalities.

In modern mass production, the question of negative externalities imposed by itself. Markets are often not able to perform efficient allocation of natural resources. These are all cases occur when external effects. The dominant conception of economists is that the mechanisms of similar market could provide efficient private and social behavior.

ECONOMIC INSTRUMENTS OF ENVIRONMENTAL POLICY

The goal to implement the environmental protection and implementation of the concept of sustainable development, inevitably raises the question of economic instruments. These are instruments that directing economic subjectivity through the internalization of environmental costs and the costs of depleting natural resources[2]. The

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[1] Petrović N., *Ekološka svest kao osnova održivog razvoja*, IV skup privrednika i naučnika, Zbornik radova "Menadžment, tehnologije i inovacija", novembar, Beograd, 2006., str. 220-221.

[2] Panayotou T., *Instruments of Change –Motivating and Financing Sustainable Development*, UNEP, Earthscan Publication, 1998.

use of these instruments does not act directly on the implementation of a different technology or environmental standards, but the economic irregularities seek to correct the instrument.

Economic instruments Environmental Protection to twenty years ago were used only in exceptional cases because their use is met with strong opposition and with the industry and the public. However, the requirements for achieving "sustainable" development sought to create new types and forms of instruments, which would work on global pollution.

Economic instruments are one of the groups of instruments in the field of environmental protection, which aims to achieve certain environmental improvements. The main purpose of the application instrument is economic to provide for adequate determination of the price of organic-natural resources, in order to ensure their efficient use and correct allocations. If you get a real ecological resource, adequate price, like any other good, it can be expected that their treatment will then be like any other factor of production, including the efficient allocation of scarce resources.

In the market economy, environmental protection can be achieved:

- positive preventive actions to reduce pollutants and especially elimination of pollution;
- accountable public life of the community (especially local and regional Communities).

Economic instruments should contribute as much as possible the integration of environmental policy with other policies. In particular, it relates to a system of proper pricing of environmental resources, which should lead to easier fitting of environmental policy in the entire fiscal system and price. In order to ensure effective private and social behavior are the following economic instruments:

• Fees and taxes on emissions. Fees for emissions are direct payments based on estimates or actual measurements of the concentration and type of emissions. In countries in transition, is usually related to a large number of manufacturers and are often combined with penalties.

• User fees and taxes. This instrument has a local character. The funds raised in this way are used to finance concrete environmental problems localities disposal and waste collection, treatment of municipal water, exploitation of raw materials, hunting grounds, parks, ponds and the like. The centralized revenue, which primarily is not intended to protect the environment, but also increase local government revenues and just taxes.

• Penalties. Taxes and penalties are the simplest mechanism. When production caused negative external effect, correct the sentence, or tax, manufacturers face the social consequences of its economy. The purpose of this instrument is to equalize private and social costs and benefits. When the manufacturer of fines in the amount of marginal costs of pollution, the marginal private and social costs will be compensated. The manufacturer can reduce pollution by reducing or manufacturing methods. Changes in the method of manufacture may result in expenditure on equipment to control contamination, or to change the input (raw material).

- Fees for products. Products that cause environmental pollution during the production, consumption or in the form of waste, burdening the estimated social costs. The aim is to adjust the relative prices of products, in order to reduce their demand, but also raised funds serve the amended financing mode of production, that is environmentally friendly.
- Warranty execution. Manufacturers and users of natural resources, are obliged to deposit guarantee, which guarantees compliance with the requirements of environmental protection. After the applied execution obligations, the guarantee is returned to the manufacturer.
- Damages. For the operation of this economic instrument, it is necessary that the role of the state has an obligation to create and guarantee the right to compensation or damages through the regulation of funds (funds for water pollution, endangering biodiversity funds, funds for oil spills, etc.). Reimbursement refers to cases where the dominant part of the revenue used to cover costs and protecting the environment (for example, funds are raised through funds for the protection of water and environment).

The negative effects of economic instruments must be neutralized:

- specifying exemptions in exactly the prescribed limits, and
- providing subsidies in a certain amount.

Among the economic instruments are expected to be effective instruments of protection and preservation of the environment, is expected to provide the initiative for innovation in the protection and preservation of the environment.

In addition to economic instruments for environmental protection, there are still regulatory instruments, as well as their combination with the instrument of public opinion and the internalization of the costs of protecting and preserving the environment.

ECONOMIC INSTRUMENTS OF ENVIRONMENTAL POLICY IN TRANSITION COUNTRIES

The main advantage of economic instruments is that they incorporate environmental needs directly into the mechanism of market prices. The effectiveness of economic instruments for its flexibility given pollutants as a basis for creating a consumer-like effective strategy. Ecological contributions such as tax collection and direct payment by the polluter.

Proposals for expanded use of economic instruments to tackle pollution was partly blocked in transition countries, due to the existing regulatory institutions. What we expect is the objective that the transition should enable the integrated use of economic instruments for this purpose.

What is interesting for countries in transition is that a large number of investments in environmental purposes actually goes to investment in technologies for waste water treatment and general waste management problems. National sources of funding for the costs of the public sector including local government revenues, transfers from the central state budget and "soft loans" from the ecological funds. Many countries in transition have included the private sector in public infrastructure projects and environmental protection, through various forms of partnerships.

One of the most important institutional change is the decentralization of power and responsibility. In the case of public environmental services, it is much more likely to come to the overlap between local needs and offer services. However, there are certain drawbacks of decentralization:

- many local authorities have experience and knowledge in the implementation of the ecological system management;
- have sufficient financial resources to carry out the responsibilities given downloaded areas.

Environmental protection is not based on market principles, ie the price of this protection may not reflect the scarcity of resources or ensure their optimal allocation, as is the case with the "ordinary" goods and services on the market.

Funds for the environment play an important role in financing the costs of environmental protection. The fund normally used for investments reducing pollution of air, water, and waste management. This is done mainly in two ways: direct financial support to users (businesses, municipalities and other institutions), and through an intermediary role by mobilizing financial resources from other sources for co-financing infrastructure projects with an impact on improving the environment. Funds are very important policy instruments in the transition process because they are directly involved in securing investment for improving the environmental situation. In most countries in transition funds are legal entities that earn income from the prescribed fee, and are in varying degrees, under the supervision of the Ministry of Environment.

CONCLUSION

The main objective and the task of the economy in relation to the environment is reduced to the finding of such procedures and methods that will, through the production process, ensuring the most effective possible, "processing" of natural resources into goods and services to meet some of the many human needs. In contrast, the main "interest" ecology, also in order to meet certain human needs, is that the natural environment, with all its resources, preserve unaltered. Confrontation of the objectives of economy and ecology from the perspective of the use of the natural environment and its resources, predominantly expressed through the opposition of environmental principles and measures of protection of the environment and application markets, as well as the mechanism of allocation of social resources that benefit the economy.

Juxtaposition of economy and ecology, practically, is reduced to the problem of finding and implementing such allocation mechanism social (and natural) resources, which will, along with the implementation to their primary function as a maximization of the (economic) efficiency, and the allocation, and to provide the maximum preservation of the ecological balance.

Theoretically, if the plan is implemented as the sole and exclusive mechanism for the allocation of all resources of a society, "conflict" between the need for "economic exploitation" and "environmental impunity" of the environment and its resources would appear to be less pronounced, at least from the standpoint of uniformity of use mechanism for allocation of the total social resources.

REFERENCES

1. Bogdanović S., *Zaštita životne sredine Republike Srbije – Između politike i prakse približavanja EU*, Novi Sad, 2008.
2. Drašković B., *Ekonomija prirodnog kapitala*, Institut ekonomskih nauka, Beograd, 1998.
3. *Environmental financing in Centarl nad Eastern Europe 1996-2001.*, Regional Environmetal Center.
4. Panayotou T., *Instruments of Change –Motivating and Financing Sustainable Development*, UNEP, Earthscan Publication, 1998.
5. Petrović N., *Ekološka svest kao osnova održivog razvoja*, IV skup privrednika i naučnika, Zbornik radova "Menadžment, tehnologije i inovacija", novembar, Beograd, 2006., str. 220-221.
6. Vukićević M., Ekonomija životne sredine, Pravni fakultet, Univerzitet u Novom Sadu, 2000.

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APPLICATION OF A NEW SURFACTANT SENSOR, BASED ON FUNCTIONALIZED MWCNTs, FOR THE DETERMINATION OF ANIONIC SURFACTANTS IN MUNICIPAL WASTEWATERS

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ABSTRACT

The application of a new anionic surfactant sensitive sensor containing multi-walled carbon nanotubes noncovalently functionalized with tetraoctadecylammonium tetraphenylborate for the potentiometric determination of ASs content in municipal wastewaters was described.

The two titration modes (DET and MET) were investigated. The obtained recoveries ranged between 73.8 and 94.4% for the DET mode and from 87.3 and 103.8% for the MET mode indicating remarkable higher accuracy achieved using MET mode. The end point volumes were reliable estimated from the first derivative curves by using the Savitzky-Golay-Barak method. A satisfactory agreement between standard MBAS method and MET mode was obtained.

Key words: surfactant sensor, municipal wastewater, potentiometric titration, MET mode, DET mode.

INTRODUCTION

Detergents are widely used in households and industry. The most important ingredients of detergents are surfactants who's annual production is growing 4,4% and it is estimated that it will be in 2021 about 40 billion USD worth. [1] Depending on their electrochemical nature when dissolved in water, there are four main types of surfactants: anionic, cationic, non-ionic and amphoteric. Due to their physicochemical characteristics, anionic surfactants (ASs) are often used as main ingredient in detergents, although they found the application in pharmaceutical industry, agriculture, cosmetic industry etc. Their wide application in various products makes ASs the mostly used group of surfactants. [2] Linear alkylbenzene sulfonates (LAS) and alkylbenzene sulfonates (ABS) are ASs that have been most commonly used in detergent industry.[3] Because of toxicity of LAS and ABS to aquatic life, fast and accurate determination of ASs is of great importance. [4,5] Two obsolete methods, Methylene Blue Active Substances method (MBAS) and two-phase titration are still used as standard methods for determination of ASs in spite of many shortcomings. [6,7]

An excellent substitute for standard methods are ion-selective electrodes (ISE), which application in ASs determination is continuously increasing.

Therefore the design of the surfactant sensors and membrane compositions are constantly modifying in order to enhance the analytical properties of sensor [8-13].

In these investigations anionic surfactant determination in municipal wastewaters was described using a new sensitive surfactant potentiometric sensor. The difference between two modes of potentiometric titration of low level anionic surfactants as well as their methods of end point location was presented.

MATERIALS AND METHODS

Materials

Potentiometric titration: cetylpyridinium chloride (CPC) (Merck, Germany), sodium dodecyl sulfate (NaDS) (Fluka, Switzerland). For pH adjustment in real samples hydrochloric acid (HCl) (Carlo Erba Reagent, Italy) was used.

MBAS method: chloroform ($CHCl_3$) (Fisher Scientific, UK), methylene blue (Kemika, Croatia), sulfuric acid (H_2SO_4) (Kemika, Croatia), buffer solution pH = 10 (sodium hydrogencarbonate $NaHCO_3$ and anhydrous sodium carbonate Na_2CO_3) (Kemika, Croatia).

All solutions were prepared with deionized water.

Apparatus

Potentiometric titrations: Titrando 808, 806 Exchange unit, 801 stirrer and 826 mobile pH meter (all from Metrohm, Switzerland), software Tiamo (Metrohm, Switzerland).

MBAS method: Spectrophotometer UV-VIS 1700 Pharmaspec (Shimadzu, Japan)

Surfactant potentiometric sensor (FCNSS): noncovalently functionalized multi-walled carbon nanotubes (MWCNTs) with tetraoctadecylammonium tetraphenylborate (TODA-TPB). [14]

Measurements

Potentiometric titrations: the samples of municipal wastewaters were filtered and diluted with deionized water. The pH of samples was adjusted to 3. The solution of CPC ($c = 1 \cdot 10^{-4}$ M) was used as the titrant. The program for potentiometric titration was set to Dynamic Equivalence point Titration mode (DET mode) or Monotonic Equivalence point Titration mode (MET mode), the signal drift for both measurement modes was set to 5mV/min.

MBAS measurements were accomplished according to the ISO standard method.

RESULTS AND DISCUSSION

The samples of municipal wastewaters were titrated using CPC ($c = 1 \cdot 10^{-4}$ M) as the titrant and the new FCNSS sensor as an end-point detector. The two titration modes were used, DET and MET mode. The standard addition method was applied to check the accuracy, precision and to evaluate the influence of matrix. The resulting titration curves are shown in Figure 1.

By DET mode the volume of titrant increments were variable, depending on the course of titration. At the beginning of titration procedure the increments were larger and by approaching to the equivalence point they became smaller and smaller. After the equivalence point they became larger again. By MET mode the volume of titrant increments were constant, but selectable during all the titration procedure.

As it can be seen from Figure 1, the titration curves exhibited less pronounced inflexions in both titration modes. The automatic titrator could not identify end point in any mode.

In Figure 2 the first derivatives of the titration curves from Figure 1 are displayed. The end point volumes by all titrations were estimated from the first derivative curves.

The end points of titration curves with slightly pronounced inflexions can be reliable determined from the derivative curves using the extension of the Savitzky-Golay method, developed by Barak [15], with statistical testing of additional terms of polynomial degree leading to an adaptive-degree polynomial filter, which selects the lowest polynomial degree that is statistically reasonable. Figure 3 demonstrates the application of Savitzky-Golay method, modified by Barak (Savitzky-Golay-Barak method, SGB method), where the clear pronounced maxima on the first derivative curve was obtained enabling reliable end point detection. The end point can be also located from the second derivative curve, where the end point was easily determined as the intersection of the second derivative curve and X-axis.

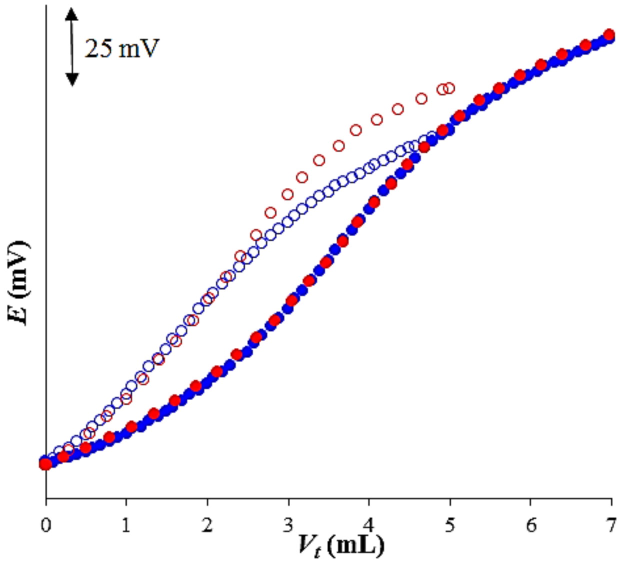

Figure 1. The titration curves of a municipal wastewater in MET and DET mode with the addition of known amounts of DS (c = 1 · 10^{-4} M) obtained using CPC (c = 1 · 10^{-4} M) as the titrant and the new FCNSS as an end point detector. (○ MET mode; ○ DET mode; ● sample + DS, MET mode; ● sample + DS, DET mode).

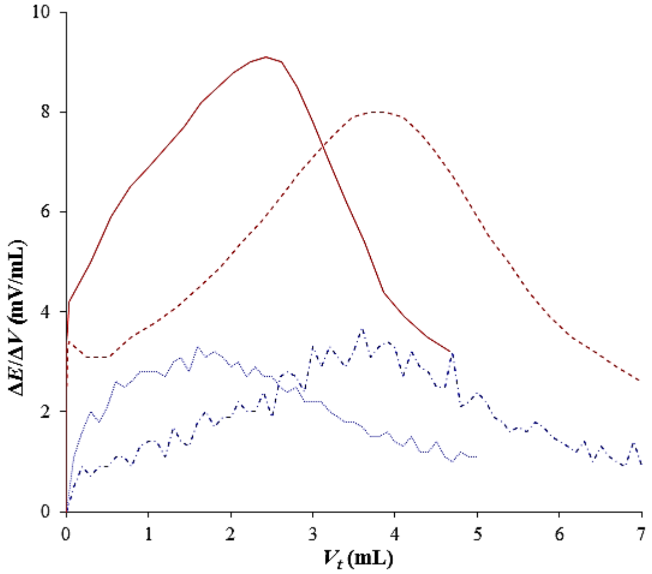

Figure 2. The first derivatives of titration curves of a municipal wastewater in MET and DET mode with the addition of known amounts of DS (c = $1 \cdot 10^{-4}$ M) obtained using CPC (c = $1 \cdot 10^{-4}$ M) as the titrant and the new FCNSS sensor as an end point detector. (···· MET mode; — DET mode; —·— sample + DS, MET mode; --- sample + DS, DET mode).

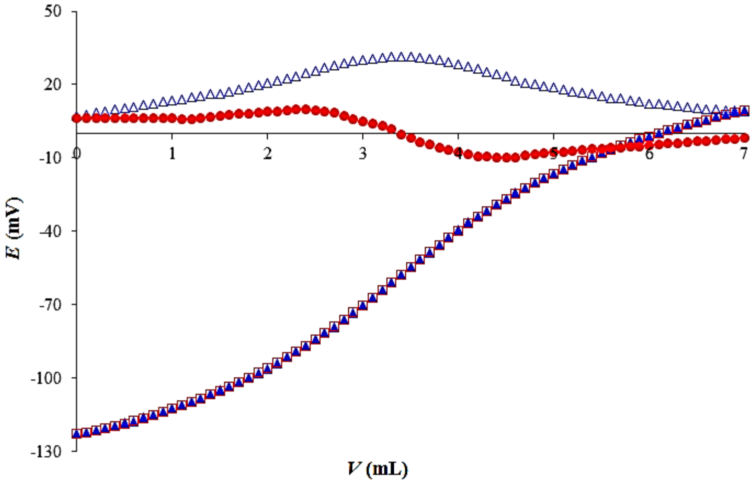

Figure 3. The titration curve of a municipal wastewater in MET mode obtained using CPC (c = $1 \cdot 10^{-4}$ M) as the titrant and the FCNSS sensor as an end point detector, and its first and second derivative after smoothing procedure according to SGB method. (▲ titration curve E = f(V); □ smoothed titration curve; Δ the first derivative; ● the second derivative).

The results of determination for three samples of municipal wastewastewaters, taken from different locations are shown in Tables 1 (the results obtained using DET mode) and 2 (the results obtained using MET mode).

The calculated recoveries ranged between 73.8 and 94.4% for the DET mode and from 87.3 and 103.8% for the MET mode. It can be concluded that the significant difference in accuracy was observed between the both, DET and MET mode. It can be seen that remarkable higher accuracy was attained using MET mode.

Table 1. Results and statistics of potentiometric DET mode of anionic surfactants in municipal wastewaters obtained using CPC (c = 1 · 10^{-4} M) as the titrant and the new FCNSS sensor as an end point detector.

Wastewater sample	AS found [mol L^{-1}] ± RSD [%][a)]	NaDS added [mol]	NaDS found [mol] ± RSD [%][a)]	Recovery [%][a)]
1	2.60 · 10^{-5} ± 5.9	2.00 · 10^{-7}	1.89 · 10^{-7} ± 5.6	94.4
2	2.49 · 10^{-5} ± 5.1	2.00 · 10^{-7}	1.41 · 10^{-7} ± 1.9	70.4
3	5.48 · 10^{-6} ± 6.7	2.00 · 10^{-7}	1.48 · 10^{-7} ± 3.1	73.8

[a)] average of 5 determinations

Table 2. Results and statistics of potentiometric MET mode of anionic surfactants in municipal wastewaters using the CPC (c = 1 · 10^{-4} M) as the titrant and the new FCNSS sensor as an end point detector.

Wastewater sample	AS found [mol L^{-1}] ± RSD [%][a)]	NaDS added [mol]	NaDS found [mol] ± RSD [%][a)]	Recovery [%][a)]
1	2.76 · 10^{-5} ± 3.1	2.00 · 10^{-7}	2.08 · 10^{-7} ± 5.0	103.8
2	1.65 · 10^{-5} ± 4.5	2.00 · 10^{-7}	1.81 · 10^{-7} ± 3.5	90.4
3	3.55 · 10^{-6} ± 11.9	2.00 · 10^{-7}	1.75 · 10^{-7} ± 3.6	87.3

[a)] average of 5 determinations

The results of the both, MET and DET modes were compared with those obtained using standard spectrophotometric MBAS method and the results are shown in Table 3. A very satisfactory agreement between MBAS method and MET mode was obtained. The results obtained by the DET mode deviated strongly from those obtained by MBAS method and MET mode.

Table 3. The comparison of results of anionic surfactants content in municipal wastewaters obtained using potentiometric DET and MET mode and MBAS method

Wastewater sample	AS content using MWCNT-TODA-TPB sensor [mg L^{-1}] and MET mode	AS content using MWCNT-TODA-TPB sensor [mg L^{-1}] and DET mode	AS content using MBAS method [mg L^{-1}]$^{b)}$
1	9.64	9.06	9.82
2	5.75	8.68	5.63
3	1.24	1.91	1.40

CONCLUSION

A new anionic surfactant sensitive sensor containing multi-walled carbon nanotubes noncovalently functionalized with tetraoctadecylammonium tetraphenylborate, was used for the potentiometric determination of ASs content in municipal wastewaters. The two titration modes (DET and MET) were investigated. The resulting titration curves exhibited a slight pronounced inflexion, thus showing the need for finding a methodology for reliable end point evaluation. The end point volumes by all titrations were estimated from the first derivative curves by using the extension of the least-squares regression formalism of the Savitzky-Golay-Barak method. The standard addition method was applied to check the accuracy, precision and to evaluate the influence of the matrix.

The remarkable higher accuracy was attained using the MET titration mode. The results obtained by the DET mode deviated strongly from those obtained by MBAS method and MET mode

The satisfactory agreement between the results obtained using standard MBAS method and those obtained by MET titration mode was evidenced.

Acknowledgements

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REFERENCES

1. Acmite Market Intelligence, (2016), Market Report, Global Surfactant Market, 4th ed., Ratingen, Germany
2. Cserhati, T., Forgacs, E., Oros, G., (2002), Biological activity and environemtal imapct of anionic surfactants, Environment International 28, 337-348, Elsevier
3. Akyuz, M., Roberts, D. J., (2002), Determination of Linear Alkylbenzene Sulphonates and their Biodegradation Intermediates by Isocratic RP-HPLC, Turkish Journal of Chemistry 26, 669-679, Tübítak Academic Journals

4. Scott, M. J., Jones, M. N., (2000), The biodegradation of surfactants in the environment, Biochimica et Biophysica Acta 1508, 235 – 251, Elsevier
5. Ivanković, T., Hrenović, J., (2010), Surfactants in the environment, Arhiv za higijenu rada i toksikologiju 61, 95 – 110, Institute for Medical Research and Occupational Health, Zagreb
6. International Organization for Standardization, *Water quality, Determination of surfactants, Part 1: Determination of anionic surfactants by the methylene blue spectrometric method, ISO 7875/1*, Geneva, Switzerland, 1984.
7. International Organization for Standardization, *Surface active agents, Detergents, Determination of anionic-active matter by manual or mechanical direct two-phase titration procedure, ISO 2271*, Geneva, Switzerland, 1989.
8. Galović, O., Samardžić, M., Derežić, D., Madunić-Čačić, D., Sak-Bosnar, M., (2012), Potentiometric titration of micromolar levels of anionic surfactants in model effluents using a sensitive potentiometric sensor, International Journal of Electrochemical Science 7, 1522-1531, ESG publisher
9. Sak-Bosnar, M., Matesic-Puac, R., Madunic-Cacic, D., Grabaric, Z., (2006), New potentiometric sensor for determination of low levels of anionic surfactants in industrial effluents, Tenside Surfactants Detergents 43, 82-87, German Chemical Society
10. Madunić-Čačić, D., Sak-Bosnar, M., Samardžić, M., Grabarić, Z., (2009), Determination of anionic surfactants in industrial effluents using a new highly sensitive surfactant-selective sensor, Sensor Letters 7, 50-56, American Scientific Publishers
11. Samardžić, M., Galović, O., Hajduković, M., Sak-Bosnar, M., (2017), A novel, fast responding, low noise potentiometric sensor containing a carbon-based polymeric membrane for measuring surfactants in industrial and environmental applications, Talanta 162, 316-323, Elsevier
12. Samardžić, M., Galović, O., Petrušić, S., Sak-Bosnar, M. (2014), The Analysis of Anionic Surfactants in Effluents Using a DDA-TPB Potentiometric Sensor, International Journal of Electrochemical Science 9, 6166-6181, ESG publisher
13. Galović, O., Samardžić, M., Petrušić, S., Sak-Bosnar, M., (2015), Application of a New Potentiometric Sensor for Determination of Anionic Surfactants in Wastewater, Chemical and Biochemical Engineering Quarterly 29, 307-313, Croatian Society of Chemical Engineers
14. Petrušić, S., Samardžić, M., Széchenyi, A., Sak-Bosnar, M., (2017), Application of a new functionalized MWCNTs for the construction of surfactant potentiometric sensors, submitted for publication
15. Barak, P. (1995), Smoothing and Differentiation by an Adaptive-Degree Polynomial Filter, Analytical Chemistry 67, 2758-2762, American Chemical Society Publications

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IMPORTANCE OF SAFE DISPOSAL OF ANIMAL BYPRODUCTS IN ENVIRONMENT PROTECTION

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ABSTRACT

Agricultural and food industry by-products, if not valorized, are disposed on landfills, in lagoons, buried in arid terrains or in open water courses, thus contaminating the environment. The importance of harmless removal of animal wastes increases with the intensification of animal breeding and with development of meat processing plants. Nowadays, it has a big role in environment protection. Application of biofuels contributes to reduction of oil consumption (i.e. of imports), reduction of emissions of detrimental gases, stimulation of sustainable development of rural regions and increasing of available quantities of high-quality animal feed. If all mentioned ecological and economical aspects are recognized properly, it becomes clear that organized solving of safe disposal of inedible by-products obtained from slaughtered or died animals by their technical processing is a valuable task. This contributes to prevention of spreading of contagious diseases, to prevention and rehabilitation of the environment and to rational use of waste materials.

Key words: by-products, harmless removal, environment.

INTRODUCTION

Under industrial conditions of slaughtering of swines, beef cattle and poultry inedible by-products are obtained besides the meat. A number of these by-products have potential to be used as feed ingredients of animal origin and technical fat. This topic attracted attention of many researchers. Solution for the problem on harmless removal of wastes of animal origin has gone through different stages and was always closely linked to diseases of animals and people, as well as to environmental protection. According to Regulation EU 1069/2009, inedible by-products from healthy cattle that do not have nerve tissues (blood, tabular and tubular bones, ribs) may be prepared as feed for pets [1].

For better utilization of raw materials of animal origin, better performance of technological processes and production of the high-quality products, good knowledge of raw material characteristics is necessery. Studying the structure and parameters to be used for calculation the potential amount of animal waste, stated that the processed by-products from slaughtered animal represent nutrient-rich feed suitable for animal[2].

Quality of products obtained by processing of animal wastes depends largely on the composition of initial raw material. Nutritional caracteristics as well as other indicators of quality are determined by, first of all, the content and composition of nutrients in initial raw material[3]. Examining the quality of raw materials suitable for the technical processing of feed for animal feeding, Ristic et al. determined that the protein feed produced from slaughterhouse by-products is an excellent source of protein of high biological value. According Gómez-Juárez et al., inedible by-products of slaughtered pigs contained significant amount of essential amino acids and vitamins suitable for feeding poultry[4]. Park at al., found that the collagen of bone and tendon collagen contained 22,2 and 33,0% glycine as opposed to muscle protein that it contained only 5%[5].

In order to identify the application value of by-products generated at swines slaughtering, the aim of this study was to determine chemical and nutritional characteristics of such materials. furthermore, the goal was to point out the content of nutritive substances that could enable better understanding of the quality of the available raw materials of animal for production of high-quality protein and energy feed and their inclusion in pet food [2]

MEAT INDUSTRY BYPRODUCT

Fundamental task of agriculture is the production of adequate quantities of high quality foods and raw materials of organic origin for the existing World's population and for high increasing of that population of about 93 million people per year. Even growing demands for food production impose the needs of more efficient managing with economic resources that such one production follows. Management with agricultural resources is crucial for survival of mankind, i.e. for the economic, cultural and social development of the society [6].

Safe disposal of the inedible animal wastes is considered as irreplaceable veterinarian-sanitary and preventive measure in suppression of spreading of infective diseases of animals and human beings. Even more and more is emphasized its role in rehabilitation and protection of the environment. Meat industry are important linker of food production chain. Together with intensification of the production process and with production of the even larger quantities of meats, emerge the problems of dead animals and of accumulation of slaughter house wastes.

Solution of the problem on harmless removal of waste products of animal origin, have exceptionally economic important, today, it is unreplacable veterinarian-sanitary and preventive usage in suppression catlle infections and zoonoses, and special attention is paid to environment protection and rehabilitation.

Table 1. Slaughter and animal byproduct quantities in the Republic of Srpska. 2016. (Statistical Office of the Republic of Srpska)

Origin of wastes	**Slaughter, pcs**	**Byproduct, t**
Cattle	32 865	1 472
Swines	76 953	553
Sheep	8 501	61
Poultry	754 5310	4 527
TOTAL		6 613

Quantity of animal wastes which are appeard in circulation of goods (raw meat, intestines, cured products, sausages, fat) as well as quantity of died animals corpses which can be collected, should be added on this quantity. If the production of livestock and meat industry are not going to change drasticty, there are cca 7.000 t of the animal by-products annualy or cca 23,5 t daily, which should be harmless removed [7].

IMPORTANCE OF SAFE DISPOSAL OF ANIMAL BYPRODUCTS

Necessity of solution of safe disposal of animal byproducts by their utilization with processing into animal feed and bioenergents, grows with the intensification of animal growing and the increasing of capacities of industrial slaughterhouses, uprising of new small slaughterhouses, building of plants for meat processing and increasing of the volume of international trade of commercial animal products. Correct solution of safe disposal of animal by-products can be perceived with three key aspects that should fulfill the technological solutions for solving of disposal of such materials by their processing, namely: with the epidemiologic-epizoothiologic aspect, with aspects of environment protection, and economic aspect.

Without any doubt, the newest and the best method of safe disposal of animal wastes is their technical processing in separate categories into products for chemical industry, bio-fuels and feed for definite kinds of animals. Prerequisite for safe disposal of animal wastes using one of the described methods is organized collection and delivery of raw materials. Modern disposal of waste materials demands orderly constructed plants with adequate capacities, which should assure permanent and continuous supply of raw materials. This confirms the importance of recognizing of the raw materials fundaments for each object, i.e. organizing of epizoothiologically and economically acceptable region, which should enable obtaining of adequate quantities of animal wastes that should allow designing and construction of modern object for their safe disposal.

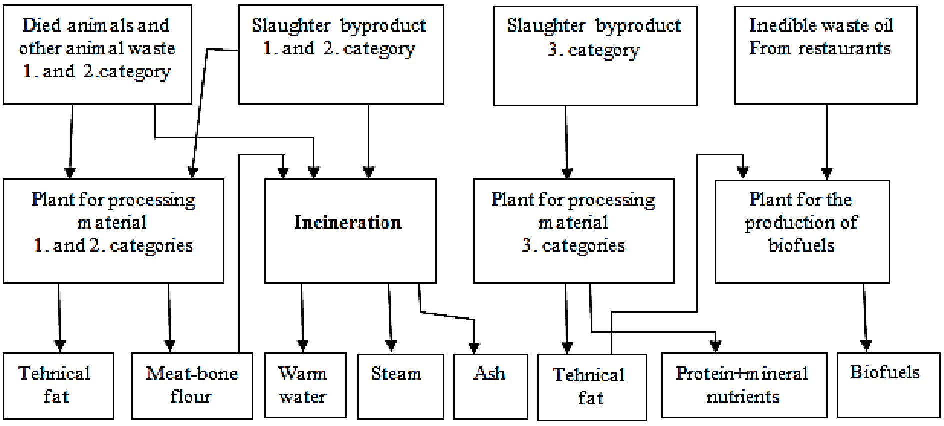

Figure 1. Organizing of collection storaging and safe disposal of animal wastes

In such collecting circle, organizing of collection of animal wastes represents very delicious problem, from whose solution to a very high degree depends the successful operation of the plant that is going to process such raw materials. This problem in any case has to bother both plant that process raw materials of animal origin or cattle growing farms and slaughterhouses that generate such raw materials. Also, important role in solving of the problem have local municipal communities. They are, according the existing legislative rules on suppression of contagious diseases, obliged to organize safe disposal of animal wastes in their region. In other words, organization of collecting of mentioned raw materials should be based on contractual linking of plants for safe disposal and processing of animal wastes and local municipal communities or their corresponding organizations (slaughterhouses, animal farms etc.).

Exceptionally important is to emphasize the necessity of transferring of animal wastes from the place where they were generated to the storaging place as fast as possible, as well as the necessity of rapid performing of the procedure of their processing. This is very significant, not only from the epidemiologic-epizoothiologic aspect or from environment protection aspects, but equally from the aspect of their technical processing. Namely, fresh raw materials are processed easier, with generation of lower quantities of waste gases and obtaining of better quality products.

Economic side of this problem implies collection and safe disposal of huge quantities of biological materials that necessitate costs, which have to be incorporated in prices of the obtained products. If wastes of animal origin were not processed (recycled), they represent lost raw material that was possible to incorporate in production of proteinaceous - energetic feed, technical fat for chemical industry or of fuels with high calorific value.

According to the European Union directives included in the Regulation (EC) N^{o} 1609, with processing of sanitary safe inedible by-products obtained during slaughtering of animals (materials Category 3), it is possible to obtain[8]:

- proteinaceous, protein-mineral and energetic products aimed for animal feeding,
- technical fats,
- feathers for textile industry,
- skins, horns, hoofs, hairs,

and from died animals (materials Category 2):

- meat-and bone meal as an energent,
- technical fat as an energent or raw material for further processing in chemical industry of for production of bio-diesel, and
- biogas, compost.

We shall mention only that with the respecting procedures of blood collection and its technological processing various articles for human use can be obtained, primarily products, which are used as functional additives in manufacturing of meat products. Special processing procedures enable their use as raw materials in pharmaceutical industry or for production of functional foods.

On the other hand, industrial waste blood can be collected and processed using corresponding technological procedure in a plant for processing of other animal byproducts, using special processing unit. Such one procedure enables obtaining of feed with high protein content, which, mostly, contains high quantities of essential amino acids, vitamins and mineral substances, and particularly iron [9].

Safe disposal of the described animal wastes (material Category 1) by combustion on high temperatures (over 850°C) enables obtaining of warm water or steam as an energent for processing plant that use warm water or steam, and ash as construction material for roads. Articles (meat- and bone meal and fat) obtained by processing of materials of Category 1 are suitable for use as energetic fuel, i.e. as fuel for direct combustion in architecturally separated objects, respecting the corresponding legislative rules.

CONCLUSIONS

1. Agricultural and food industry byproducts, if not valorized, are disposed on landfills, in lagoons, buried in arid terrains or in open water courses, thus contaminating the environment.
2. If all mentioned ecological and economical aspects are recognized properly, it becomes clear that organized solving of safe disposal of inedible by-products obtained from slaughtered or died animals by their technical processing is a valuable task. This contributes to prevention of spreading of contagious diseases, to prevention and rehabilitation of the environment and to rational use of waste materials.
3. To the most rational solutions of their disposal belong their processing into feed, or raw materials for chemical industry and production of biofuels. Manufacturing of feed from sanitary safe raw materials they are multiply valorized, with assurement of the rational development of cattle growing and of

protection of the environment. Application of biofuels contributes to reduction of oil consumption (i.e. of imports), reduction of emissions of detrimental gases, stimulation of sustainable development of rural regions.

REFERENCES

1. Okanović Đ., Ristić M., Nikolić-Stajković S. (2011). Remediation of by-products from slaughtered animals in regard to new regulations, Tehnologija mesa 52,1,31-38.
2. Ristić M., Okanović Đ., Sakač M. (2011). Karakteristike životinjskih sporednih proizvoda i njihova namena, Monografij*a*, FINS Novi Sad, broj strana 195.
3. Okanović, Đ., Ristić, M., Kormanjoš, Š., Nježić, Z., Lilić, S., Grujić, R. (2010). Chemical and nutritional quality of slaughter pigs by-products, Quality of Life*,* 1,1,55-60.
4. Gómez-Juárez, C., Castellanos, R., Ponce-Noyola, T., Calderón V., Figueroa J. (1999). Protein recovery from slaughterhouse wastes. Bioresource Technology,70,129-133.
5. Park, E., Lee, H., Song, K.B. (1996). Characterization of plasma proteins from bloods of slaughtered cow and pig and utilization of the proteins as adhesives, Agricultural Chemistry and Biotechnology,**39**,123–126.
6. Meyer R. (2007): Comparison of scenarios on futures of European food chains. Trends in Food Science & Technology, 18 (11) pp. 540-545.
7. Đukić V., Okanović Đ. (2012). Bezbjedno uklanjanje otpadaka animalnog porijekla, Acta Œcologica Academica, vol 1,112-123.
8. REGULATION (EC) No 1069/2009 of the European Parliament and of the Council.
9. Đukić V., Okanović Đ. (2011) Application of best available techniques in meat Processing, Food and Feed Research, 2, 87-93

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EFFECT OF GAMMA RADIATION ON THE INACTIVATION OF AFLATOXIN IN HEMP FLOUR

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ABSTRACT

Aflatoxin is a type of mold that is considered a human carcinogen and can be found in various foodstuffs. A potential effective method in the removal of aflatoxin from food products is a gamma irradiation. Here, we investigated and established a procedure for reduction for these mycotoxins in hemp flour samples at industrial-scale gamma irradiation facility. The content of aflatoxins in the samples was analysed in a microbiological laboratory using validated standardized methodologies (DML 1.2.2016). Hemp flour samples were irradiated with gamma irradiations doses of 1, 2, 3, 4, 6, 8 and 10 kGy, and results have demonstrated that delivered dose of 4 kGy reduces the level of total aflatoxins to acceptable value according to the national legislation of Republic Serbia and European Union (Regulation on maximum residue levels of pesticides in or on food and feed of plant and animal origin [1]). The European Commission (EC) has set maximum safety limits of aflatoxins B1, B2, G1 and G2 in cereals and cereal-derived products at 4 µg/kg [2].

Key words: food, irradiation, conservation, aflatoxin, hemp.

INTRODUCTION

Industrial hemp is an annual plant, which contains less than 0.3% THC, psychoactive substances. It is an environmentally friendly plant that does not require any spray chemical preparations, and the amount of green mass is very significant, more than 10 t/ha [3]. Additionally, the cultivation of hemp brings great benefit to agricultural producers and raise their competitiveness in the market. The value of the product increases up to 10 times by processing of industrial hemp. This is a product that sells easily and demand for hemp products is increasing every year. There is the expansion of cultivation of hemp in the world, for the most diverse purposes, over 20 000 products can be produced from industrial hemp. It is significant in the textile industry, paper industry, food, pharmaceutical, cosmetics, construction, and environmental protection worldwide. The application of hemp in the industry is rapidly expanding from paper manufacturing, bio-composite materials for the automotive industry, construction industry, biodegradable plastics, bio-fuel and every day reveals the new possibility of applying [4, 5, 6].

One of the biggest problems that occur when growing hemp is the development and increased the content of mycotoxins mostly originated from soil, atmosphere, and handling. High levels of mycotoxins make hemp products potential hazards for the health of consumers and also reduces quality and shelf life of these products [7]. The species of molds that combine to form aflatoxin grow in soils when atmosphere conditions in areas with high moisture and high temperatures. The type called aflatoxin B1 is considered the most toxic, capable of causing health problems such as liver disease or cancer, autoimmune responses, digestive issues and in rare cases even death. The strains of aflatoxin most common in foods include B1, B2, G1 and G2 which have the high carcinogenic potential [8]. One of the most effective solutions to solve these problems is the application of gamma irradiation on these types of products.

Irradiation has been identified as a valid option for food processing, guaranteeing the decontamination and preserving products. Gamma rays are produced by radioactive substances (called radioisotopes) that continuously emit the high-energy gamma rays. The approved sources of gamma rays for food irradiation are cobalt-60 (the most common) and cesium-137. Energy from this radiation source is too low to induce radioactivity in any material, including food. This process is validated and regulated by international organizations such as FAO (United Nations Food and Agriculture Organization), WHO (World Health Organization), Codex Alimentarius and by the European Directives (Directive 1999/2/EC; Directive 1999/3/EC) [9, 10, 11].

When radiation energy is absorbed by food, it causes a variety of chemical and physical reactions. The amount of energy the food absorbs is controlled so the changes produced have desirable food preservation effects while maintaining the safety, quality, and wholesomeness of the food. The food itself does not become radioactive.

In this way, gamma irradiation could be used by food industry to establish a feasible procedure for plants preservation and decontamination. However, this method must be validated for each matrix since the results vary significantly with the type of food, radiation dose, food geometry (which affects dose uniformity), in order to understand how the major nutrients are preserved and simultaneously guarantee the microbial decontamination.

The aim of this work was to determine the delivered dose of gamma radiation which would significantly reduce the content of aflatoxin in hemp flour. The effects of gamma irradiation on total aflatoxins have been studied in hemp flour samples which are collected from the Agricultural cooperative of producers and processors of alternative plant species. The content of aflatoxins was analysed in the microbiological laboratory. The obtained results in this work allow to estimate the minimum radiation dose to guarantee the disinfection and the decontamination to meet the microbiological safety criteria for foodstuffs defined by the legislation (Commission regulation EC nº 1441/2007) [12].

EXPERIMENTAL

Agricultural cooperatives *"Hemp"* have several different products from hemp. They test all the products and take all measures to ensure these products were correct when packed in containers to the store. Figure 1. shows samples of hemp flour from the manufacturer Agricultural cooperatives "Hemp".

Figure 1. Samples of hemp flour from the manufacturer Agricultural cooperatives "Hemp"

Gamma irradiation is a physical method based on the ability of high-energy photons generated by radioactive ^{60}Co, to induce chemical DNA damage in biological contaminants such as insects, molds, yeasts and bacteria. The gamma sterilization process in "Vinča" Institute of Nuclear Sciences uses cobalt-60 radiation for research and industrial irradiation, for radiation sterilization of medical devices, pharmaceutical and as well as for microbial decontamination of herbs and spices and a variety of different products. Doses of gamma radiation of 1, 2, 3, 4, 6, 8 and 10 kGy were applied on hemp flour samples. Figure 2. shows samples prepared for gamma irradiation processing.

Figure 2. Sampling and preparation of hemp flour for gamma irradiation processing

Dosimetry measurements of absorbed doses were performed using the ethanol-chlorobenzene solution (ECB) dosimetry system which provides a reliable measurement in materials [13]. The ECB solution is well-known reference standard dosimeter for evaluating absorbed dose [14,15]. Measurements were made by oscillotitrator OK-302/1 supplied by Radeliks Electrochemical Instruments, Budapest. Absorbed dose is determined through measurement results and the calibration curve. Calibration curve is performed using EBC dosimeters irradiated at High Dose Reference Laboratory of Risø National Laboratory, Denmark.

The microbiological parameters evaluated total aflatoxins (B1, B2, G1 and G2). The evaluation of the microbiological parameters was performed before and after irradiation treatments based on the validated methodologies (DML 1.2.2016).

RESULTS AND DISCUSSION

The results of microbiological tests of hemp flour samples before irradiation treatment are presented in Table 1.

Table 1. The results of microbiological tests of contaminated hemp flour samples before irradiation treatment

	samples					**Method**
	1	2	3	4	5	
total aflatoxins (B1, B2, G1 and G2) [µg/kg]	28.0	27.5	27.5	28.0	29	DML 1.2.2016

These samples were exposed to different doses of gamma irradiation 0 – 10 kGy. It is observed that irradiation has significantly reduced the level of total aflatoxins in the samples. The influence of the radiation dose on the content of total aflatoxins is shown in Figure 3.

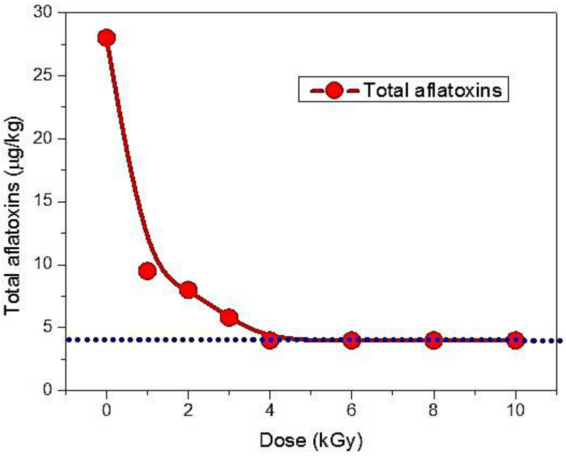

Figure 3. Reduction of total aflatoxins in hemp flour samples exposed to different doses of gamma irradiation

It was confirmed that the delivered dose of 4 kGy is quite sufficient to reduce the aflatoxin content in all samples to an acceptable value of 4 µg/kg. Also, this dose is completely safe for the reduction of these kinds of total aflatoxins. Reduction of these mycotoxins affects the extension of the shelf-life of hemp flour because there will be no deterioration in quality.

CONCLUSIONS

Gamma irradiation has become effective of processing and preserving food products. In this paper has been successfully established an effective dose of gamma radiation that is needed for reducing aflatoxin content in order to hemp flour to be microbiologically safe for further use and consumption. It is shown that delivered irradiation dose of 4 kGy significantly reduces the aflatoxin content in all samples of hemp flour enabling in this way the extension of their shelf-life.

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REFERENCES

1. European Commission, Commission Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC, Text with EEA relevance, 2005
2. European Commission, Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, Text with EEA relevance, 2006
3. Swanson, T, Controlled Substances Chaos: The Department of Justice's New Policy Position on Marijuana and What It Means for Industrial Hemp Farming in North Dakota, North Dakota Law Review, 90 (3), p. 613, 2015
4. Deitch, R, Hemp: American History Revisited: The Plant with a Divided History, p. 219, Algora Publishing, 2003
5. Wesley, T, Re-defining Environmental Harms: Green Criminology and the State of Canada's Hemp Industry, pp 528-554, Canadian Journal of Criminology & Criminal Justice, 57 (4), 2015
6. Keller, N, The Legalization of Industrial Hemp and What it Could Mean for Indiana's Biofuel Industry, p. 555, Indiana International & Comparative Law Review, 23 (3), 2013
7. Molins, R, Food Irradiation, Principles and Applications, pp 1-32, A John Wiley & Sons, inc. publication, 2001

8. Kanapitsas, A, Batrinou A, Aravantinos A, Markaki P, Effect of γ-radiation on the production of aflatoxin B1 by Aspergillus parasiticus in raisins (Vitis vinifera L.), pp 327-332, Radiation Physics and Chemistry, Volume 106, 2015
9. World Health Organization, Wholesomeness of irradiated food, pp 7-13, WHO, Geneva, Switzerland, 1981
10. CODEX STAN 106-1983, rev.1-2003. General Standard for Irradiated Food, pp 1–3, Vienna, Austria
11. European Parliament, Council of the European Union, Directive 1999/2/EC. (22 de February de 1999). Directive of the European Parliament and of the Council. OJ L 66 of 13.03.1999. 16 – 23
12. European Commission, Commission Regulation (EC) No 1441/2007, amending Regulation (EC) No 2073/2005 on microbiological criteria for foodstuffs, Official Journal of the European Union, 2007
13. ISO/ASTM 51538 - Practice for use of the ethanol-chlorobenzene dosimetry system,International Organization for Standardization, 2009
14. Razem, D, Dvornik, I, Application of the Ethanol-Chlorobenzene Dosimeter to Electron-Beam and Gamma-Radiation Dosimetry: II Cobalt-60 Gramma Rays, pp. 405–419, IAEA Symposium on Dosimetry in Agriculture, Industry, Biology, and Medicine, Vienna, 1972, IAEA, Vienna, 1973
15. Kovács, A, Stenger, V, Fóldiák, G, Evaluation Methods of the Ethanol-Monochlorobenzene Dosimeter System, pp. 701–709, 6th Tihany Symposium on Radiation Chemistry, Vol II, Hedvig, P., Nyikos, L., Schiller, R. eds., AkademiaiKiado, Budapest, 1987

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GAMMA IRRADIATION OF LEATHER GLOVES IN TERMS OF CULTURAL HERITAGE PRESERVATION

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ABSTRACT

Microorganisms, fungi, and insects are often present in many types of cultural goods, from the immovable objects, through archival and library materials, cellulose tape of film materials, studio paintings, articles of wood, textiles, leather, and other museum objects. The biocide effect of the ionizing radiation can be effectively implemented for their removal. The objective of this work is the conservation by gamma irradiation of objects from the Museum of Nikola Tesla, which is of outstanding value. In this case, infected leather gloves are irradiated with a dose of 5 kGy to eliminate mold. The amount of mold was evaluated by microbiological analysis before and after gamma irradiation treatment. After successful treatment, Tesla's leather gloves are preserved from further deterioration and are now displayed in the museum.

Key words: cultural heritage, gamma irradiation, conservation, leather.

INTRODUCTION

Nowadays, increased concerns regarding the safeguarding of patrimony result in the constant evolution of conservation and restoration methods. Biodeterioration is one of the most challenging issues that curators have to deal with. The materials organic matter (paper, textile, wood, leather, etc) is susceptible to degradation by insects, fungi, molds, bacteria, which inhabit and feed on these materials. In recent years the storage of objects of cultural heritage has become a major problem all over the world due to changes in the microclimate, especially due to the change of climatic conditions, increased the content of moisture in the air as well as the temperature, which is susceptible to the development of said pests. Improper storage conditions lead to massive biological attacks in museums, archives or libraries, which are difficult to stop or eliminate because of the large quantities of items involved. In addition, these microorganisms may present serious health hazards for people dealing with CH artefacts [1, 2].

High energy radiation is a powerful tool for disinfection, effectively used in many fields, especially for sterilization of medical products. Irradiation techniques are being used to protect and preserve works of art around the world. The techniques are supported by the International Atomic Energy Agency (IAEA) [3], which operates projects to preserve cultural heritage artefacts using radiation. Wooden items, film archives, documents, textiles, leather, parchment even mummies can be attacked and destroyed by bacteria, fungi, mould and insects [4,5,6]. These items can be brought from churches, museums and conservation centres to irradiation facilities where it could be treated with gamma rays, however, it has not been widely used for that purpose, although there is a great need for this kind of technique. Compared to other techniques, gamma irradiation treatment is very high-level effectiveness and reliability and has a major advantage: the biocide effect is ensured by the radiation's high penetration power. Also, removing bio-deteriorating agents, stopping the ongoing destructive process, restoring the object of cultural value. The wider use of this technique requires conclusively establishing that irradiation does not lead to unacceptable changes in the functional or decorative properties of the CH artefacts. Regarding requirements of effectiveness within ethical guidelines such as minimal intervention, non-contact irradiation techniques is very attractive. Besides, it enhanced by penetration power of gamma rays that provides an interesting way to reach the inside of 3-dimension items.

The effectiveness of ionizing radiation on bio-deteriogen organisms has been further confirmed as well as the need to further study on the radio-induced effects. On the basis of physical and microbiological obtained results, a dose of treatment ranging from 5 to 7kGy has been recommended to obtain a significant reduction of the microbial load with minimum negative effect on the paper substrate [7].

Nikola Tesla Museum in Belgrade is conceived as the establishment of a complex institution with cultural, educational, scientific and memorial character. This item is largely determined by his original vision and mission. As a cultural institution, the Museum dedicated to the protection and presentation of Tesla's legacy and this cultural heritage is an invaluable [8].

The objective of this work is the conservation and preservation of objects from the Museum of Nikola Tesla, in this case, the leather gloves. It is important to emphasize that these high contaminated objects represent a potential threat to nearby objects or a collection depot where they are located. On the surface analysed gloves present dispute mass (millions) 2-5 μm size. These spores are extremely light, dry quickly and effectively transmitted through the air and colonize the surrounding objects. Transmission is multiplied during the manipulation of infested items. These items were subjected to gamma irradiation in order to disinfection. The radiation dose that is delivered is determined based on the comprehensive analysis of the results of microbiological laboratories, material composition, as well as the condition of subjects and literature data based [9]. After the performed treatment, it confirmed that it has successfully carried out disinfection of infected objects, and they are again exposed in the museum.

EXPERIMENTAL

The subjects of the leather gloves were brought from the Nikola Tesla Museum (Figure 1).

Figure 1. Samples of Nikola Tesla leather gloves highly contaminated with mold

The gamma sterilization process in "Vinča" Institute of Nuclear Sciences uses cobalt 60 radiation for research and industrial irradiation, for radiation sterilization of medical devices, pharmaceutical and as well as for microbial decontamination of herbs and spices and the variety of different products. Processing with gamma rays yields quick turnaround time, easily penetrating packaging and product and is cost-effective. Dosimetry measurements were performed using the ECB dosimetry system which provides a reliable means of measuring absorbed dose in materials [10].

The microbiological parameters evaluated: total counts, molds and yeasts counts detection. The evaluation of the microbiological parameters was performed before and after irradiation treatments based on the validated methodologies. The characterization of herbs microbiota was performed by conventional microbiological techniques in order to define a contamination pattern and identify the major microbiological contaminants.

RESULTS AND DISCUSSION

Microbiological analyses were done and it was identified two types of xerophile fungi of the genus Aspergillus: Aspergillus halophilicus (teleomorph: Eurotium halophilicum) and Aspergillus penicillioides. According to contemporary literature that studies the deterioration of buildings and objects of cultural heritage of these two species are listed as very destructive and deterioration responsible for the degradation of objects built from the leather (analysed books with leather covers) (Figure 2).

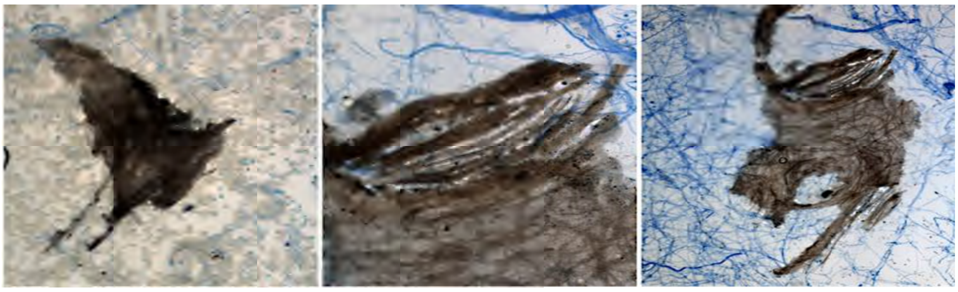

Figure 2. Degraded fragments of leather

In addition to the leather of these two types of substrates are significant for all the dry substrates, as these are the fungi xerophilic, respectively preferred are materials with a low content of the active water. These fungi do not require a high water content of the substrate, on the contrary "choose" the dry material and are highly adapted to the dehydrated conditions where successful invasive colonize objects containing cellulose and protein fibers (such as books, leather straps, all items of the skin, the layer of paint of paintings, the back of the picture). Our experience shows that these kinds of causes of the phenomenon of "foxing" (appearance of brown spots on the leaves of books, bindings, and especially on the back of the linen cloth paintings).

These samples were exposed to the dose of gamma irradiation of 5 kGy in order to destroy the microorganisms which exist in the samples. Effect of the radiation dose is to destroy entire contents of micro-organisms which were confirmed by microbiological analyses that are made after the completion of treatment. Samples of leather gloves after irradiation treatment are shown in the picture (Figure 3). This dose of gamma irradiation obtains a significant reduction of the microbial load with minimum negative effect on the substrate.

Figure 3. Samples of Nikola Tesla leather gloves after the performed treatment. Gloves are decontaminated, preserved from further deterioration, and are now displayed in the museum

CONCLUSION

The application of irradiation treatment for the protection of cultural heritage artefacts was made possible by the development of radiation processing procedures. In this paper has been successfully established an effective dose of gamma radiation that is needed for reducing the microbial load with minimum negative effect on the substrate. It is shown that delivered irradiation dose of 5 kGy destroys the microorganisms which exist in the samples.

Acknowledgements

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REFERENCES

1. IAEA TECP-RER 8/015, Nuclear techniques for preservation of cultural heritage artefacts, 2009.
2. IAEA Radiation Technology Series 2, Nuclear Techniques for Cultural Heritage Research, 2011.
3. IAEA Nuclear Techniques for Cultural Heritage Research, IAEA RADIATION TECHNOLOGY SERIES No. 2, 1-224, International Atomic Energy Agency Vienna International Centre, 2011
4. Razem, B, Razem D, Braun, M, Irradiation treatment for the protection and conservation of cultural heritage artefacts in Croatia, Radiation Physics and Chemistry, Volume 78, Issues 7–8, July–August 2009, Pages 729–731
5. Bicchieri, M, Monti, M, Piantadina, G, Sodo, A, Effects of gamma irradiation on deteriorated paper, Radiation Physics and Chemistry, Volume 125, August 2016, Pages 21–26
6. Chio, J, Lim, S, Inactivation of fungal contaminants on Korean traditional cashbox by gamma irradiation, Radiation Physics and Chemistry, Volume 118, January 2016, Pages 70–74
7. M. Adamo, S. Baccaro, A. Cemmi Enea, Radiation Processing For Bio-Deteriorated Archived Materials And Consolidation Of Porous Artefacts, Unità Tecnica Tecnologia dei Materiali Laboratorio Tecnologie di Irraggiamento Centro Ricerche Casaccia, Roma, RT/2015/5/ENEA
8. http://nikolateslamuseum.org/web/pages.php?p=4
9. Stanculescu, I, Moise, V, Ponta, C, Haiducu, M, Nisipeanu, S, Geba M, Miu, L, Iordache, O, Gamma irradiation a chance for textile and leather heritage artefacts' conservation, Proceedings of the Balkan Symposium on Archaeometry Proceedings of the 29-30 October 2012 Bucharest, Romania
10. ISO/ASTM 51538 - Practice for use of the ethanol-chlorobenzene dosimetry system, International Organization for Standardization, 2009

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BUSINESS GUIDE ACCORDING TO THE LAW ON CHEMICALS (CHEMICALS RISK MANAGEMENT)

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ABSTRACT

Chemicals have a wide range of potential negative effects, from health risks like carcinogenicity, and physical effects such as flammability, to organic ones such as widespread contamination and toxicity to aquatic life.

However, although significant progress has been made in recent years when it comes to regulation and management of chemicals, and even though governments, employers and workers continue with their efforts to minimize negative effects of application of hazardous substances both at national and international levels, it is still insufficient. Serious incidents continue to occur and there are still negative impacts on the human health and environment.

The most important international source of information on chemical safety is the Globally Harmonized System of Classification and Labeling of Chemicals (GHS). GHS has been designed to cover all chemicals including pure substances and mixtures, and to set conditions for notification in case of chemical risks in the workplace, risky goods transport, consumers and the environment. As such, it is a truly harmonized and universal technical system with a far-reaching impact on all national and international regulations for chemical safety. GHS has a list of criteria for classification according to health, physical and environmental risks.

Key words: management of chemicals, chemical safety, GHS.

INTRODUCTION

Chemicals are of vital environmental importance, and their benefits are widespread and recognized. From pesticides that have an increasing impact on the amount and quality of food production, to pharmaceutical products that treat diseases, and cleaning products that help in the establishment of hygienic living conditions, chemicals are essential for healthy and modern lifestyle. Chemicals are also a key part of industrial processes in developing the products that are important for global environmental standards. However, controlled exposure to these chemicals in the workplace, as well as their limited emissions into the environment, are tasks for which solutions the government, employers and workers are constantly trying to find.

Chemicals are used for almost every type of workplace and therefore a wide range of workers is potentially exposed. While the amount of effort needed to solve specific situations depends on the degree of exposure and the quantity handled, there is no sector that can simply be exempted from mandatory prevention and control of hazardous substances. Toll of occupational diseases caused by exposure to chemicals is very high. Beside the possibility of serious injuries and illnesses of workers who handle chemicals in the workplace, there is also a possibility of damage to the building and in the worst case, impact to the community in the region and the environment in general.

The overall strategy to achieve the proper management of chemicals in the workplace and the environment can be easily explained as follows: first step is to identify chemicals that are present, then classify them according to health, physical and environmental risks. The next step is the preparation of the code and safety sheets for the communication of risks and related protection measures.

The second step is to assess how the identified and classified chemicals are used in the workplace, and what exposure can result from such use. This can be achieved through exposure control and the third and final step is to use this information to prepare appropriate preventive and protective programs in the workplace. This includes different types of preventive and control measures, introduction and application of technical control, substitution of chemicals with less hazardous ones, and the use of respiratory care and other personal protective equipment when necessary. [1-7]

Other provisions of detailed programs that support and enhance this kind of control is exposure monitoring, information and training of exposed workers, records, medical surveillance, planning for emergency situation and disposal procedures.

For many years, chemical waste from facilities has been randomly dumped into the ground, air, and water in a particular area. This situation has changed greatly in those countries where adequate control and practice of clearing and preventing such occurrences have been established.

While the use of chemicals in working processes is just a step, proper disposal and management of emissions and discharges are also important.

DISCUSION

Why the Law on Chemicals has been introduced and what is its purpose? Establishment, maintenance and improvement of a unified chemicals management system in Serbia

Ensuring the highest level of protection of human health and environment and improving free movement of chemicals with the EU and other countries. Ensuring competitiveness of economy and encouraging development of safer alternatives.

Law on Chemicals has been aligned with many EU laws, as follows:

Regulation 1906 / 2006 – registration, evaluation and authorization of chemicals with REACH where possible Regulation 67/548 / EEC on the approximation of the law, regulations and administrative provisions relating to the classification, packaging and labeling of hazardous substances.

Regulation 1999/45 / EC on the approximation of the law, regulations and administrative provisions of member states relating to the classification, packaging and labeling of hazardous preparations.

Regulation 440/2008 / EC of test methods in accordance with the Regulation 1907/2006/EC concerning the registration, evaluation and authorization of chemicals

Regulation 2004/42 / EC on the limitation of emissions of volatile organic compounds in the use of organic solvents in certain paints, varnishes and products for final machining of vehicles

Regulation 689/2008/EC concerning export and import of hazardous chemicals
Regulation 1272/2008 on classification, packaging and labeling of chemicals
Regulation 648/2004 on detergents
What have we achieved by this law?

- Integral Register of chemicals that are placed on the market, is arranged
- Classification, packaging, labeling
- Restrictions of prohibition, placing on the market and use of chemicals
- Import and export of certain hazardous chemicals
- Particularly hazardous chemicals and licenses - their use and trade
- Integrated management
- Marketing of detergents
- Monitoring of chemicals and availability of data, control, consultants, etc.

There is a Register –

Because in this way we have a better insight into chemicals that are on the market, they can be controlled, measures to reduce risk can be established, public informed, it can be reacted in time of accidents.

Hazardous chemical is the chemical that can be classified in at least one class of hazards. Chemicals of concern are chemicals which on the basis of their properties represent the greatest threat to human health and the environment SVHC.

υ Particularly hazardous chemicals are chemicals classified in one of the classes of of hazards in the table, which is part of the Regulation on PHC.
υ CAS number is an identification number assigned to each individual substance which was published in the scientific literature and entered in the CAS registry (Chemical Abstract Service - CAS)
υ EC number, ie. EINECS, ELINCS or NLP code is the official identification number of a substance in the European Union.

Each hazardous chemical has its own classification and the classification is conducted in accordance with the Regulation - Purpose of classification and labeling –

υ The main objective of classification and labeling of chemicals is to ensure that users of chemicals are properly informed on hazardous properties of chemicals in order to protect human health and the environment.
υ This is achieved by establishing a legal framework that ensures the following:

1. Chemicals are classified into classes of hazards according to clearly defined criteria based on their hazardous properties;
2. Chemicals are labeled in a way that users are warned of hazardous properties of chemicals and of possible risks to health and the environment, as well as of security measures that should be taken.

Classification of chemicals into a particular class of hazards will be based on the data of their properties:

1) physical and chemical properties;
2) toxicological properties (effects on human life and health);
3) eco-toxicological properties (effects on the environment) of classification criteria in hazard classes.

During classification, the following data are used:

data obtained on the basis of results of preliminary testing; from epidemiological studies and practical experience of effects on humans (statistical data on occupational diseases and chemical accidents); literature (scientific research); experimental data obtained with the prescribed method of testing hazardous properties of chemicals; data on evaluation of hazards of a mixture obtained with the calculation method; data obtained from a validated model of qualitative or quantitative structure-activity relationship). [1-7]

Packaging material (packaging and labeling)

υ Packaging material for hazardous chemicals must match the characteristics, purpose and method of using them and must be labeled in the prescribed manner.
υ Packaging material for hazardous chemicals must be labeled so as to contain the trade name of the chemical, names of certain hazardous substances contained in the mixture, name and address of the supplier of chemicals, amount of chemicals in the packaging material and graphic displays, labels and text indicating hazardous properties of chemicals in the Serbian language. [9]

Safety Data Sheet - is the best source of information for the identification and quantification of a chemical risk in the workplace. The obligation of the employer, in case hazardous chemicals are present in the workplace, is to assess the risk by using the information on Occupational safety and health provided by the supplier, ie. safety data sheet. Supplier of hazardous chemicals may be a legal person or an entrepreneur who is a producer, importer, distributor or downstream user (professional producer of the mixture, distributors and consumers are not considered downstream users). The obligation of the supplier is to inform the next in the supply chain of hazardous properties of the chemicals which he sells or gives free of charge. This notification is called communication of hazards and can be done through a label (intended for all categories of users, but primarily for the consumer) and through a safety data sheet (intended for professional users of chemicals). Distribution method (who, whom, when) and the form of safety data sheets are very precisely formulated by the Law on Chemicals and the

Regulation on the content of the safety data sheet. This document is subject to change depending on new information on hazardous chemicals which it relates to. For this reason, the safety data sheet must have the date of creation or revision. Safety data sheet has 16 chapters very important for chemical. In first chapter there is information about Toxicology center in VMA for emergency calls. Every year there is official document that shows statistics regarding poisoning in Serbia. Based on the data for patients poisonong there are data for last 6 years, from 2010 till 2015 where we can see percents of poisonong by corosives for example, during the years. Datas are similar so conclusion is to continue to fight and finding ways to use and manipulate with chemicals with more safety so workers or users should not be in nonsafety position. Poisoning continues to be a significant cause of morbidity and mortality in the Republic of Serbia. Poison Control Centre represents a national resource to collect and monitor poisoning exposure cases and improvements of financial and personnel resources would further promote its activity. [8] Poison Information Centre is not jet adequately equipped and this would be one of the primary goals in the future. Statistic based on data regarding poisoning by corrosives is as follows in figure 1.

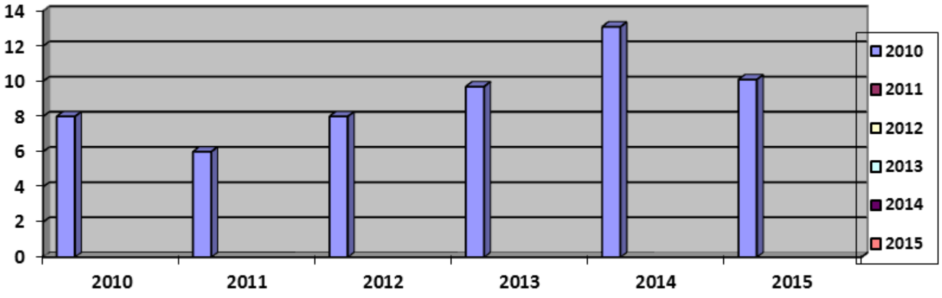

Figure 1. The yearly poisoning by corrosives on human from 2010 to 2015

CONCLUSION

Safe management of chemicals requires effective and efficient management through transparency, participation of the public and responsibility of all partners. Better social dialogue in order to improve legislation and its implementation, including efficient labor inspection, which has the necessary resources that are implemented by trained and qualified inspectors who are not improperly influenced from external parties.

Safe management of hazardous chemicals in the workplace is an essential element for reducing their impact on workers' health, industry and environment. In order to implement all this, it means the following should be done: systematic monitoring of chemicals, minimizing the risks that chemicals pose to human health and the environment;iInformation and raising awareness in industry and consumers; encouraging the introduction of safer alternatives.

It is clear that sensible use of chemicals, their controlled release into environment and their disposal is essential if we want to ensure future environmental safety and health. Also important is the development and implementation of national prevention and control strategies and systems that comprehensively and simultaneously deal with health, safety and environmental aspects related to the use of chemicals in order to ensure coordinated and sustainable management and, above all, decent jobs for all.

REFERENCES

1. The Law on Chemicals ("Official Gazette of RS" no. 25/15)
2. Regulation on the register of chemicals ("Official Gazette of RS" no. 1/15)
3. Regulation on the classification, packaging, labeling and advertising of a chemical and certain product in accordance with Globally Harmonized System of Classification and Labeling of the UN ("Official Gazette of RS" no, 105/13)
4. List of substances of concern ("Off. Gazette of RS", no. 94/13)
5. Regulation on bans and restrictions of production, marketing and use of chemicals that pose an unacceptable risk to the human health and environment ("Official Gazette" no. 25/15)
6. Regulation on particularly hazardous chemicals ("Official Gazette of RS" no. 15/13)
7. List of classified substances ("Off. Gazette of RS", no. 105/13, 48/14)
8. Regulation on keeping records of chemicals ("Off. Gazette of RS", no. 31/11)
9. Regulation on detailed conditions of keeping hazardous chemicals in the sales area and labeling the area ("Off. Gazette of RS", no. 16/12)

THE SYSTEMATIZATION OF CONTAMINATION DEGREE ASSESSMENT OF SEDIMENTS AND ECOLOGICAL RISK

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ABSTRACT

Sediments play an important role in the assessment of environmental contamination, because in pollutants, including heavy metals, can be deposited, transported, and represent a source of contamination. To monitor the impact of polluted river sediment on the environment and human health are very important information about the origin of toxic elements, their variability and potential ecological risk. The aim of this paper is to systematize and simplify the procedure for conducting the assessment of the contamination level of sediments, by statistical methods, using parameters and indices. Finally it's possible to assess the risk of contamination by heavy metals in sediments.

Key words: sediment, environmental contamination, heavy metals, ecological risk, statistical methods.

INTRODUCTION

Quality assessment and monitoring of natural flows have become a regular part of testing the quality of sediment and national plans of rivers conservation. As such, they require a lot of attention, because they represent a potential source of mobility and bioavailability of pollutants, such as trace elements in aqueous systems. Trace amounts of heavy metals are always present in fresh waters from terrigenous sources such as weathering of rocks resulting into geo-chemical recycling of heavy metal elements in these ecosystems [1, 2].

The contamination of sediments with heavy metals is a matter of great concern, because of their persistence, bioaccumulative nature and toxicity. The content of metals in river sediments primarily depends on their mineralogical composition. The primary source of metals in the sediments of the river is the geosphere, the most common processes by which they are due to these ecosystems are processes of surface decomposition. Firstly, metals in floodplain deposits can originate from two types of sources: (1) lithogenic sources, resulting in sediment concentrations being related to the processes of erosion and sedimentation of metal-bearing geological formations up stream; (2) anthropogenic sources, that is: human activities that cause elevated metal concentrations in river waters and subsequently in floodplain deposits. [3]. To identify the origin of pollutants require a thorough analysis of the composition of sediments [4]. Analysis of the sediment quality is important for several reasons: the quality of the sediment indicates the current state of the water system and can be used to detect the presence of pollutants that are not soluble, after their discharge into surface water; in the evaluation of the contamination of water environment provides a precise picture of the contamination over an extended period, so that the time trend of contamination can be analyzed on the basis of in-depth profile [5]. Examination of the distribution of elements in sediments is also important for an understanding of their behavior and transport in fluvial or aquatic environment. Polymer contamination in surface sediments has a significant impact on the quality of the aqueous environment, which can have an effect on the levels of low-sensitive members of the food chain, and as a final consequence, and effect on human health [6].

The influence of contamination with toxic elements on the quality of the river sediment may be calculated from the evaluation of the pollution index. Identifying sources of pollution can be carried out using statistical analysis. Calculated indices of contamination and the use of statistical methods are very useful for risk assessment and environmental pollution monitoring the various elements in the sediment.

APPLICATION OF STATISTICAL METHODS IN THE ANALYSIS OF SEDIMENTS

Significance of the analysis of sediment contamination by heavy metals is reflected primarily in the fact that in the hydrological cycle, less 0.1% of metal actually dissolves in water, and more than 99.9% accumulated in the sediments. Assessment of the level of contamination of aquatic ecosystems is very important not only because of their ability to accumulate metals, but also because of the possibility of pollutants release into the water, where they are a secondary source of contamination [7, 8].

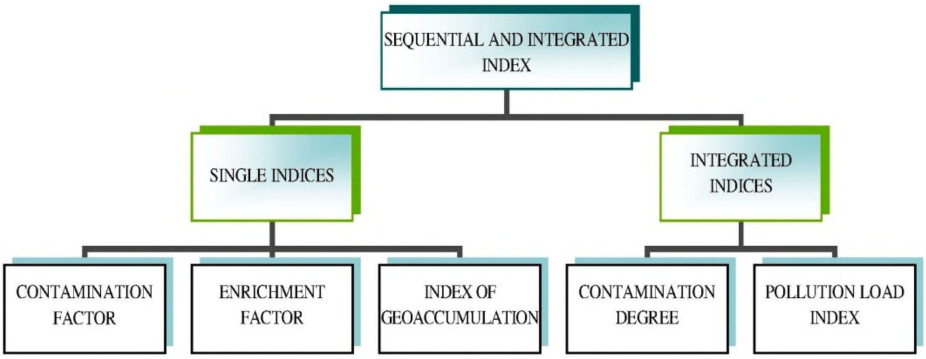

Figure 1. A schematic representation of types of indicators

Figure 2. shows the elements of assess environmental risks, and determine what is the quality of the sediment and to what extent it may affect the environment.

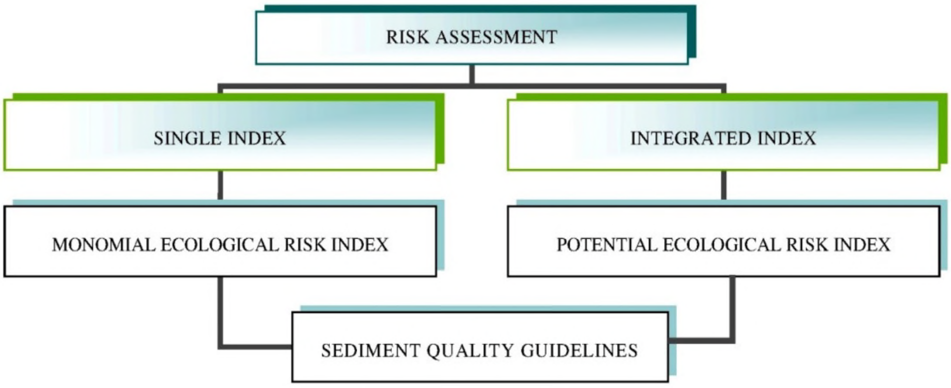

Figure 2. A schematic representation for risk assessment i.e. sediment quality guidelines

In Figure 3. are shown summarized elements which constitute steps in the methodology for characterization of sediments.

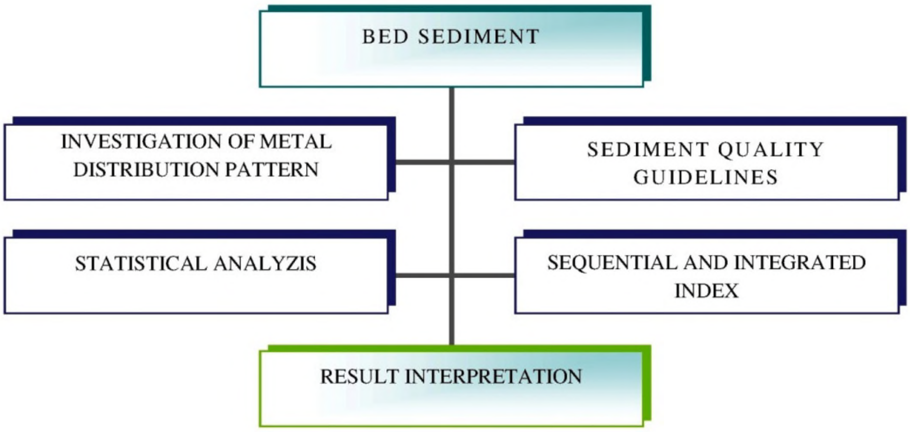

Figure 3. A schematic representation of methodology for bed sediments characterization

The aim of the method of applying a statistical analysis to process the sediment is to determine a relationship of heavy metals in sediment and surface, as well as their origin (natural or anthropogenic - Llithogenic). Indirectly in this way achieve the following objectives, in addition to this basic:

1. It is determined in the region of the level of contamination in the region by chemical fractions in order to judgeassess the quality of the water and sediments
2. The estimated environmental risk, ie. the risk of pollution
3. Allows taking appropriate measures to reduce pollution.

METHODS OF DETERMINING THE LEVEL OF CONTAMINATION OF SEDIMENTS AND ECOLOGICAL RISK ASSESSMENT

To assess the ecological status of the investigation area after contamination by heavy metals, can be used by numerous factors and indices. Some of them estimate contamination, while others estimate the potential environmental risk of toxic pollutants. Complex indices of ecological risk assessment are based on specific values which are given for each pollutant substance, towards its toxic effects.

Geochemical approaches such as the enrichment factor (EF) and geochemical index methods have been successfully used to estimate the impact of the activities of civilisation on sediments [9].

To assess the degree of contamination elements in river sediments apply: Contamination factor (Cf), Enrichment factor (EF), Index of geoaccumulation (Igeo), as well as the integrated index level of contamination (mCd) and the Pollution load index (PLI). For the assessment of the risks of contamination are determined Ecological risk factor (ERI) and Potential ecological risk index (RI).

Cf is calculated for individual items, and Cd and PLI provide general information on the contamination of sediments underlying location. Similarly Cf and Igeo [10] was calculated for individual items and provides valuable information on the degree and extent burden polluting elements in sediments. EF is used for estimating the degree of human influence of an element in the sediments of [11], as well as to distinguish between the elements originating from natural or anthropogenic activity [12]. PERI provides a mean quantitative assessment of the risk of environmental pollution caused by multiple elements in the sediments of aqueous systems [13]. It is necessary to be included in the calculation and calculation of the concentration of another element, and calculation of a potential environmental risk factors (PERI), as well as factors of sedimentary toxic responses (TRI).

The level of contamination is a form of index that aggregates all pollutants to a value based on the contamination factor (Cf). This is a reference index which is the basis for some of the later derivative index of contamination.

Modern approach to qualify the use of the modified degree of contamination (mCd), which, in 2008, proposed by Abraham and Parker, and which takes into account the number of elements (n). This index is determined in great detail, as indicated by the value of the seven levels: MCd < 1.5; < 2; < 4; < 8; < 16; < 32 and > 32, indicating nonexistentdead, is very low, low, moderate, high, very high and extremely high level of contamination of test elements [14].

Pollution load index (PLI): Tomlinson introduced the concept of the PLI to assess metal pollution and sediment [13]. The PLI for a single site is the root of the number (n) of multiple contamination factors (CF) multiplied together empirical. This index provides a simple, comparative mean for assessing the level of heavy metal pollution widely used for various water systems worldwide, thus enabling them to perform a comparison. It is based on the contamination factor (Cf). Based on the value of the index of pollution, contamination can be classified as follows: there is pollution exists, if the PLI > 1 and there is no pollution exists, if the PLI <1 [15, 16].

One approach to assess the "enrichment" of sediments by heavy metals (natural or anthropogenic) is the calculation of likelihood of enrichment (EF) for the metal concentrations that are higher than background air content elements. Although EF is not a function of time, this parameter shows the status and extent of sediment contamination of the test element [17].

Igeo, introduced by Müller, 1979, has been widely used to evaluate the degree of metal contamination or pollution and terrestrial, aquatic and marine environments and risk asessment to [18]. Sources of heavy metals in surface waters and sediments are mostly anthropogenic and very complex, but we should not neglect natural resources (as is often the case with Pb and Zn). Müller suggest seven grades or classes based on the increasing numerical value of the index Igeo [19-22].

Single-element index of environmental risk, or environmental risk factor (ERI): quantitative shows the potential environmental risk of contaminant, as shown in the work Hakanson (1980). This factor takes into account the concentrations of heavy metals and environmental factors, as well as "toxic-response" factor [23].

Potential environmental risk index (RI) is an integrated index [13, 24] and is defined as the sum of change which is an event associated with metals with respect to the content and organic sulphonic risk factor. First, the calculated risk factor for each metal, and then determines a potential environmental risk (RI), as the sum of the environmental risk factors. RI values can be ranked as follows: RI < 150; < 300; < 600 and > 600; for low, medium, high and very significant environmental risks for the basin [13]. For assessing the degree of contamination of the elements in river sediments apply: Contamination factor (Cf) Enrichment factor (EF), Index of geoaccumulation (Igeo), as well as the integrated index level of contamination (MCd) and the Pollution load index (PLI). For the assessment of the risks of contamination are determined Ecological risk factor (ERI) and Potential ecological risk index (RI).

CONCLUSION

The influence of contamination with toxic elements on the quality of the river sediment may be calculated by application of various index pollution . The identification of sources of pollution can be effected by a variety of statistical analyzes. Calculated indices of contamination and the use of statistical methods are very useful for risk assessment and environmental pollution monitoring the various elements in the sediment.

Assessment of the level of contamination of aquatic ecosystems is very important not only because of their ability to accumulate metals, but also because of the possibility of release of pollutants into the water, where they are a secondary source of contamination.

In order to simplify the procedure for assessing the level of contamination and to determine the potential environmental risks, systematic process is carried out an assessment of the contamination of sediments by means of statistical methods, and by using the parameters and indexes which monitor their condition and quantify their contamination. In this way, simply, by the steps, disclosed is a method which directly leads to the determination of the relationship of heavy metals in water and in the surface and at the same time to the sediments of determination of their origin - whether their sources are natural or man-made (lithogenic). Besides, determining the level of contamination in the region, according to the chemical fractions, and to assess the quality of water and sediments; evaluates the environmental risk, or the risk of pollution.

REFERENCES

1. Sekabira, K., Oryem, O.H., Basamba, T.A., Mutumba, G. and Kakudidi, E. (2010) Assessment of Heavy Metal Pollution in the Urban Stream Sediments and Its Tributaries. International Journal of Environmental Science and Technology, 7: 435-446
2. Mohiuddin, K.M., Zakir, H.M., Otomo, K., Sharmin, S. and Shikazono, N. (2010) Geochemical Distribution of Trace Metal Pollutants in Water and Sediments of Downstream of an Urban River. International Journal of Environmental Science and Technology, 7: 17-28
3. Vijver, M., Spijker, J., Vink, J., Posthuma, L. (2008) Determining metal origins and availability in fluvial deposits by analisis of geochemical baselines and solid-solution partitioning measurements and modelling, Environmental Pollution, 156: 832–839
4. Begum, A., Ramaiah, M., Harikrishna, Khan, I. and Veena, K. (2009) Heavy Metal Pollution and Chemical Profile of Cauvery River Water. E-Journal of Chemistry, 6, 47-52
5. Štrbac, S. (2014) Sadržaj i mobilnost teških metala i organskih jedinjenja u ekosistemu reke Tise, doktorska disertacija, s 4, Univerzitet u Beogradu, Beograd
6. Kabir, I., Lee, H., Kim, G., Jun, T. (2011) Correlation assessment and monitoring of the potential pollutants in the surface sediments of Pyeongchang River. Int. J. Sedim. Res. 26: 152-16
7. Forstner, U., Heise, S. (2006) Assessing and managing contaminated sediments: requirements data quality – from molecular to river basin scale, Croatica Chemica Acta, 79: 5–14
8. Mariani, C. F., Pompeo, M. L. M. (2008) Potentially bioavailable metals in sediment from a tropical polymictic environment – Rio Grande Reservoir, Brazil. Journal of Soils and Sediments, 8: 284–288
9. Chabukdhara, M., Nema, A.K. (2012) Assessment of heavy metal contamination in Hindon River sediments: A chemometric and geochemical approach, Chemosphere 87 pp 945-953
10. Müller, G. (1979) Heavy Metals in the Sediment of the Rhine-Changes Seity. Umschau in Wissenschaft und Technik, 79: 778-783

11. Sinex, S.A., Helz, G.R. (1981) Regional Geochemistry of Trace Elements in Checapeake Bay Sediments. Environmental Geology, **3**: 315-323
12. Olubunmi, F.E., Olorunsola, O.E. (2010) Evaluation of the Status of Heavy Metal Pollution of Sediment of Agbabu Bitumen Deposit Area, Nigeria. European Journal of Scientific Research, 41: 373-382
13. Hakanson, L. (1980) Ecological risk index for aquatic pollution control, a sedimentological approach. Water Res. 14: 975-1001
14. Abrahim, G.M.S., Parker, R.J. (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ. Monit.Assess. 136: 227–238
15. Tomlinson, D.C., Wilson, J.G., Harris, C.R, Jeffrey, D.W. (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgolander Mar. Res. 33: 566-575
16. Varol, M. (2011) Assessment of heavy metal contamination in sediments of the Tigris river (Turkey) using pollution indices and multivariate statistical techniques, J. Hazard. Mater. 195: 355-364
17. Ruzhong, L., Kun, S., Yueying, L., Yong, S. (2010) Assessment of heavy metal pollution in estuarine surface sediments of Tangxi river in Chaohu Lake basin. Chinese Geogr. Sci. 20: 9-17
18. Deming, H., Jinping, C., Xianfeng, H., Zhenyi, J., Lei, M., Hao, X., Yuning, M., Xiaojia, C., Heling, W. (2017) Spatial distribution, risk assessment and source identification of heavy metals in sediments of the Yangtze River Estuary, China, Marine Pollution Bulletin 115 (1-2) 141-148
19. Asaah, A.V., Abimbola, A.F. (2005) Heavy metal concentrations and distribution in surface soils of the Bassa Industrial Zone 1, Doula, Cameroon. J. Sci. Engin. 31: 147–158
20. Mediolla, L.L., Domingues, M.C.D., Sandoval, M.R.G. (2008) Environmental Assessment of and Active Tailings Pile in the State of Mexico (Central Mexico). Res. J Environ. Sci. 2: 197–208
21. Hacısalihoğlu, S., Karaer, F. (2016) Relationships of Heavy Metals in Water and Surface Sediment with Different Chemical Fractions in Lake Uluabat, Turkey, Pol. J. Environ. Stud. Vol. 25, No. 5: 1937-1946
22. Yukui, L., Fei, L., Xiujie, Z., Xin, W. (2017) Qingchuan, L., Pengfei, Z., Lichao, Z., Chongyu, S. Distribution and Ecological Risk Assessment of Heavy Metals in Sediments in Chinese Collapsed Lakes, Pol. J. Environ. Stud. Vol. 26, No. 1: 181-188
23. Wei, B., Jiang, F., Li, X., Li, X. and Mu, S. (2010) Heavy metal induced ecological risk in the city of Urumqi, NW China, Environ Monit Assess 160: 33
24. Yang, Z., Wang, Y., Shen, Z., Niu, J., Tang, Z. (2009) Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. J. Hazard. Mater. 166: 1186-1194

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RISK ASSESSMENT OF DDT AND METABOLITES IN WASTE AND SURFACE WATER OF NOVI SAD

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ABSTRACT

During the research carried out on the samples of wastewater and surface water of Danube screening and target analysis were performed. The samples were prepared via liquid-liquid extraction. The analysis was performed by GC-MS system. According to the results of previous sampling campaigns for the screening analysis, 69 substances were selected for target analysis, and organochlorine pesticide DDT and its metabolites have shown the most inquisitive results. The maximum detected concentrations for DDT, DDD and DDE were 500, 110 and 620 ng/L, respectively. Furthermore, risk quotient was calculated, and was higher than 1 at 8 out of 9 locations.

Key words: organochlorine pesticides, DDT and metabolites, waste and surface water, residual concentrations.

INTRODUCTION

The research was conducted during the period from 2012 to 2014 in the scope of NATO DriWAQ-NS ESP.EAP.SFP 984087, on the samples of mixed urban wastewater (WW) and surface water (SW) of Danube River, 100 m after the discharge from sewage canaling system of Novi Sad.

Having in mind that the main drinking water abstraction point is located only few hundred meters downstream of the waste water discharge points and that no urban Wastewater Treatment Plant (WWTP) in Novi Sad exists, the screening analysis represents the urgent step in order to estimate the most abundant contaminants in this part of the Danube. In the research area, 2 sampling campaign for the purpose of screening analysis and one for the purposes of target analysis were planned and executed. The screening analysis is a process of extraction, isolation, detection and identification of substance or a group of substances within a minimum number of steps and relatively short period of time for complex sample matrix as waste and surface water. Target analysis is the analytical approach where target analyte or group of substances is selected, usually from previously obtained results from screening analysis, to be analysed.

Serbia is in the implementation process of the European Water Framework Directive (WFD) whose major goal is to secure the "good chemical and ecological status" of the rivers and lakes. In the Directive on environmental quality standards in the field of water policy (2008/105/EC) Annual Average Environmental Quality Standards (AA EQS) are determined as well as maximum allowable concentrations (national legislation - *by-Law "Regulation of limit values for priority and hazard priority pollutants for surface water and deadlines" Official Gazette of* RS, no. 35/2011), shown in Table 2. DDT is one the substances elaborated and shown on the list of priority and priority hazardous substances (Annex II Directive 2008/105/EC), as well as in Annex B of Stockholm Convention.

DDT (dichlorodiphenyltrichloroethane) is the most used organochlorine pesticide before it was globally banned in the 1970s. During World War II it was used for malaria vector control and for agricultural applications, as the result malaria is eradicated from Europe, Canada and USA.

DDD (dichlorodiphenyldichloroethane) is the first metabolic product of DDT. It residual concentrations are still found around the globe as a product of decomposition of banned DDT. *DDE (dichlorodiphenyldichloroethylene)* is second metabolite of DDT also detected in various matrixes due to previous use of DDT.

DDE is especially hazardous as it is liposoluble and is hardly eluted from organisms, with the exception during lactation. It has a high potential for bioaccumulation and biomagnification.

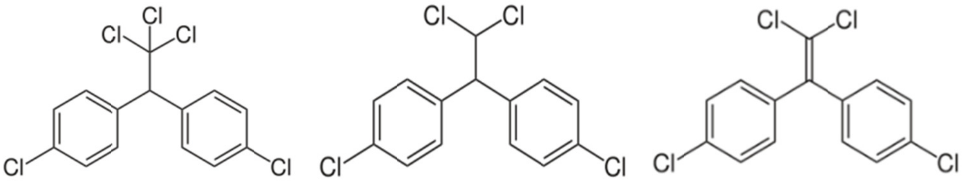

Figure 1. Structural formula of DDT, DDD and DDE

MATERIALS AND METHODS

According to the wastewater canaling map 9 sampling locations were selected.

Sampling locations with GPS coordinates, codes and water sample types are shown in Table 1 and Figure 2.

Table 1. Selected sampling sites with grid references

Location	*Cod*	*N. longitude*	*E. latitude*	*Sample type*
Alas Island	RI	45°13’54,2"	19°50’44,6"	SW
Collector Zeppelin	GC1’	45°15’3,7"	19°51’18,3"	WW
Zeppelin	GC1˝	45°15’5,4"	19°51’22,5"	SW
Collector Belgrade Bank	GC2´	45°15’44,2"	19°51’22,2"	WW
Belgrade Bank	GC2˝	45°15’43"	19°51’27,1"	SW
Collector War Island	RO´	45°15’23"	19°54’39,9"	WW
War Island	RO˝	45°15’13,4"	19°54’38,5"	SW
Collector Roko’s Creak	RP´	45°14’56,7"	19°53’43,7"	WW
Roko’s Creak	RP˝	45°15’0,5"	19°54’11,3"	SW

The catch samples from every sample locations were transported to Laboratory in portable refrigerators on 4 °C, and stored until preparation and analysis.

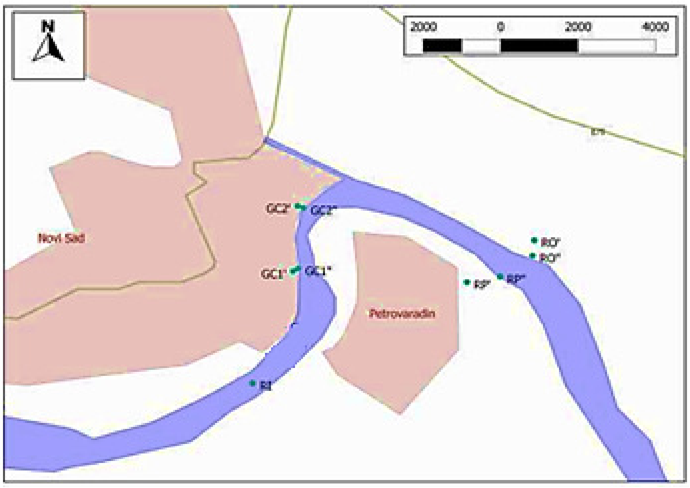

Figure 1. Map of the sampling sites

Samples were taken into the plastic bottles and stored for 48 h on 4 °C. Substances were extracted from water using liquid-liquid extraction (LLE).

LLE was conducted according to laboratory procedure: a 1L aliquot of water sample was spiked with an internal standard (PBDE-138) and extracted with 2 portions of solvent (50 mL) for 30 minutes using automatic shaker device at 700 rpm.

Extracts were concentrated by Kuderna Danish apparatus. The temperature of evaporation was set according to boiling point of solvent used during preparation. All collected extracts were evaporated to final volume of 1 mL.

The GC-MS screening analysis was performed using Agilent 6890 gas chromatograph coupled to the Agilent 5973 mass spectrometric detector. The GC system was equipped with the programmed temperature vaporization (PTV) injector, known to be suitable for large volume samples, that was raised from 60 to 260 °C at the rate of 40 °C/min. The analysis was performed on a 30 m x 250 mm I.D., 0.25 mm df DB-XLB and HP-5MS capillary column. The oven programme was formed accordingly to utilized solvent, from 40 to 60 °C, with hold time for 10 minutes for solvent delay. Helium was used as a carrier gas.

The mass selective detector (MSD) was used in the SIM mode for all the samples, and every substance was identified via 2 qualifying and 1 quantitation specific basic ions. Limits of detection (LOD) for DDT, DDD and DDE were 10, 25 and 25 ng/L, respectively [1, 2, 3].

According to EU guidance, risk assessment and impact is presented as risk quotient (RQ), calculated via equation 1. The RQ is calculated using MEC (Measured Environmental Concentration) or PEC (Predicted Environmental Concentration) values, and PNEC (Predicted No-Effect Concentrations) [4].

If RQ is higher than 1 there is a possible risk for the environment. PNEC values for DDT and its metabolites DDE and DDD, are 0.18, 0.6 and 0.64 ng/L, respectively [5].

$$\mathrm{RQ} = \frac{\mathrm{MEC\ (PEC)}}{\mathrm{PNEC}} \qquad 1.$$

The derivation of PNECs is required for the chemical safety assessment (CSA) of substances with yearly circulation of 10 t or more (REACH, ECHA) [6].

The PNECs are usually deriving by using mortality (LC50 - Median Lethal Concentration/Median Effective Concentration), growth and reproduction (ECx (the concentrations at x % effect were observed) or NOEC (No Observed Effect Concentration) typically in units mg/L or mg/kg [7].

RESULTS AND DISCUSSION

Wastewater (communal and industrial) is directly discharged into the Danube River from Novi Sad sewage canaling system.

According to the results of the screening analysis, 69 substances were selected for target analysis. Out of 69 selected organochlorine pesticide DDT and its metabolites have shown the most inquisitive results.

Table 2. Concentrations of DDT and metabolites (ng/l)

Substance	p,p'-DDT	p,p' -DDD	p,p'-DDE	ΣDDT
AA-EQS	*10*	*10*	*10*	*25*
RI	<10	<25	80	80
GC1'	260	230	80	570
GC1"	310	400	25	735
GC2'	<10	240	80	320
GC2"	<10	<25	n.d.	<25
RO'	500	620	110	1230
RO"	<10	220	80	300
RP'	<10	220	80	300
RP"	<10	<25	<25	<25

Detected concentrations of DDT are unusual for a substance that is globally banned for use in any human activity. The concentrations of DDT ranged from less than 10 (LOQ) to 500 ng/L on sampling location RO'. The occurrence of DDT in waste and surface water on locations GC1', GC1'' and RO' suggest the illegal use of this substance.

According to the detected concentrations of DDD the historic pollution is confirmed, as the concentrations throughout the whole sampling area are more or less in constant around 220 – 240 ng/L, except on the locations GC1'' (400 ng/L) and RO' (620 ng/L).

The range of DDE concentrations are almost constant throughout the whole sampling area around 1255 km of Danube, ranging from less than 25 (LOQ) to maximum of 110 ng/L. The DDE is the metabolite of DDT and its concentration before city of Novi Sad was relatively low, 80 ng/L. Accordingly, the historic pollution is confirmed.

The special attention that this data is implying is that all the detected and measured concentrations were above the AA EQS limits, which are set low as the substances are banned for over 40 years, making the situation particularly alarming.

As it was expected, after the calculation of RQ (shown in Table 3), DDT and its metabolites have a high risk onto the environment although these substances are banned for use from 1970s.

Table 3. Calculated values of RQ

Substance	RI	GC1'	GC1"	GC2'	GC2"	RO'	RO"	RP'	RP"
DDT	0	0	> 1	> 1	0	0	> 1	0	0
DDD	> 1	> 1	> 1	> 1	0	> 1	> 1	> 1	0
DDE	> 1	> 1	> 1	> 1	0	> 1	> 1	0	> 1

CONCLUSIONS AND RECOMMENDATION

Detected concentrations of DDT are unusual for a substance that is globally banned for use in any human activity. The high concentrations of DDT in waste and surface water on locations GC1', GC1'' and RO' suggest the illegal use of this substance. According to the detected concentrations of DDD and DDE, the historic pollution is confirmed, as the concentrations throughout the whole sampling area are more or less in constant. As it was expected, after the calculation of RQ (shown in Table 3), DDT and its metabolites have a high risk onto the environment as the PNEC values are low, as the substances are banned for use in 1970s. The impacts and stress of wastewater onto the natural recipient, in this case Danube River, is significant as the wastewater is directly discharged without any previous treatment. The obtained information about concentration levels of DDT and its metabolites further emphasizes the need for specifically and precisely designed wastewater treatment plant equipped with advanced treatment processes. This type of research was carried out for the first time in Serbia.

Acknowledgment

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REFERENCES

1. Sremački et al. Fres. Enviro. Bull. 25 (11) 2016
2. Vojinovic Miloradov et al. Fres. Enviro. Bull. 23 (9) 2014
3. Sremački et al. 21st ISAEP, ISBN 978-963-306-507-5, Szeged
4. Milanović et al. Serbia Chem. Soc., 80(3) 2016
5. https://circabc.europa.eu/webdav/CircaBC/env/wfd/Library/framework_directive/thematic_documents/priority_substances/supporting_substances/monitoring-based/07_Annex%20VII_PNEC_Candidate-substances.pdf
6. REACH, European Chemical Agency, https://echa.europa.eu/regulations/reach
7. Guidance on information requirements and chemical safety assessment, https://echa.europa.eu/documents/10162/13632/information_requirements_r10_en.pdf

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SUSTAINABILITY ANALYSIS OF A PHOTOVOLTAIC PANEL RECOVERY PROCESS

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ABSTRACT

In Europe, installed photovoltaic panels are about 70% compared to the rest of the world. To assemble a photovoltaic panel, several materials such as copper, gallium, indium, silicon, cadmium, aluminum, glass and end of life are needed, disposed of, becoming potentially toxic and environmentally hazardous. The effective and sustainable demanufacturing of these components is very far. In this document, we pay attention to the recycling of these products using the Life Cycle Assessment (LCA) method to calculate the environmental sustainability of an innovative process for recycling photovoltaic panel in silicon: the cryogenic process.

Key words: Photovoltaic panels, LCA, sustainability, recycling.

INTRODUCTION

The problem of how to dispose of exhausted photovoltaic panels is very important, because if they are brought to landfills or incinerated, they cause high environmental damage. With the recycle process, it is possible safeguarding the environment and the human health, and to recover of materials that in many cases have a high economic value. The cryogenic process is based on thermo-mechanically induced delamination, that is, is based on a methodology that provides for the exploitation of the different thermal expansion characteristics of the plastic material adjacent the rigid components. The basic idea is to minimize the effort in recycling the value material by adopting thermo-mechanical treatment that does not destroy subcomponents. The idea is still under a pre-industrialization study. An example of an application of the process according to the present invention is one that provides for the recovery of the electronic-grade silicon present within a photovoltaic module.

MATERIALS AND METHODS

LCA has been standardized by the ISO 14040 series, namely: ISO 14040: 2006, Principles and framework (ISO, 2006a)[6]; and ISO 14044: 2006 – Requirements and guidelines (ISO, 2006b)[7].

State of art

Literature studies contain little information on the environmental impacts created by the recycling processes of photovoltaic panels. The study carried out by Frisson (2000) [4] determined the energy consumed by a photovoltaic standard (polycrystalline silicon) and compared it to a module using recycled wafer. The researched have shown that recycled wafer has an impact per kWh of electricity produced by 40% less than the first one. However, the study does not provide information on the technique used to disassemble the module during recycling. A study by Klugmann-Radziemska and Ostrowski (2010)[5] noted that chemical treatments used in the recycling process contain high concentrations of toxic substances and require expensive disposal methods. In addition, studies on the sustainability of photovoltaic panel production processes in many cases do not consider EoL end-life passages and recycling. A study by Frankl (2005)[2] found that the disposal of photovoltaic panels affects 4% of greenhouse gas emissions considering the entire life cycle of the product but does not say which EoL discovery process is being used. The Muller study (2005)[8] provides end-of-life sustainability analysis of multi-silicon panels using the recovery process: Deutsche Solar. The process separates the silicon wafer to reuse them in the construction of new panels. Finally, the Fraunhofer Institute (2012)[3] carries out an LCA analysis on silicon-fiber recycling, with a low-impact process but not recovering precious metals. Few LCA studies on photovoltaic panel recovery consider alternative processes, for example we can mention Held (2011)[9] using the "First Solar" technique, consisting of a series of mechanical and hydrometallurgical treatments. In conclusion, most recovery processes for these products are still being developed and refined.

Goal, functional unit and system boundary

The aim of this study is to estimate the potential environmental impact of the cryogenic recovery of photovoltaic panels. Functional unit is 8.8 kg of 20 c-Si photovoltaic module modules. The system boundary is "gate to gate", ie the processes considered are: manual disassembly, mechanical thermal treatment (cryogenic), chemical treatment.

General data and assumptions, LCI

The cryogenic process analyzed separates the wafer in its constituent elements such as: Copper, Aluminum, Glass, Ethylene Vinyl Acetate (EVA), silicon, with the aim of obtaining materials with a good degree of purity in order to be re-used in other production processes as raw material. Photovoltaic panels are assumed to be transported to the recycling facility with trucks (average distance 100 km). The disassembly is manual, this process retrieves the outer part of the aluminum module, the copper cabling cables. The subsequent thermo-mechanical treatment needs energy (0.0027 kWh) and 40 liters of liquid nitrogen. Subsequently, the "chemical treatment" process is carried out with a mixture of: nitric acid, hydrofluoric acid, acetic acid, water. The waste water from the plant and the energy required for the transport trolleys and the mechanical stirrers are not considered.

Cryogenic process technology

The innovative process for the recycling of silicon PV panel [1], consists on a sequence of physical (mechanical and thermal) treatments followed by acid leaching and electrolysis. A methodology that relies on the exploitation of different thermal expansion properties of plastic materials adjacent to rigid components (mono-polycrystalline or amorphous in the case of photovoltaic panels) and the different ductility/Brittleness curves that produce controlled thermo-mechanical delamination effect. In this case the process provides for the recovery of the electronic-grade silicon present within a photovoltaic module. The process involves the following steps: 1. temperature stabilization and homogenization for a given time of all the component layers to be treated so that all the layers reach the same cryogenic temperature by placing said component in a conditioned environment; 2. imposing cycles of swift or super-swift cooling of the photovoltaic module and in particular of the layers adjacent to the semiconductor material layer, by means of a cryogenic cooling system. This latter provides the continuous control of the flow rate and pressure of a cold carrier by means of a fluid compressor or other suitable system offering the possibility of temperature conditioning; 3. A warming phase realized by a selective system, providing heat to the high conductive layer without heating the adjacent layers which are of low thermal conductivity; 4. induction of a final delamination by means of suitable systems and a mixture of liquids at a controlled pressure and flow rate. A final insufflation phase, where the process continues with a mechanical separation phase of layers with respect to the semiconductor material layer.

Table 1. Environmental impacts ReCiPe Method

Category	Value	Unit
ReCiPe Endpoint (I,A), human health, particulate matter formation[RER]	1,05	points
ReCiPe Endpoint (I,A), human health, photochemical oxidant formation[RER]	0,000445	points
ReCiPe Endpoint (I,A), human health, climate change, human health[RER]	3,28	points
ReCiPe Endpoint (I,A), human health, ionising radiation[RER]	0,00804	points
ReCiPe Endpoint (I,A), human health, total[RER]	4,55	points
ReCiPe Endpoint (I,A), human health, human toxicity[RER]	0,208	points
ReCiPe Endpoint (I,A), human health, ozone depletion[RER]	0,000408	points
ReCiPe Endpoint (I,A), resources, metal depletion[RER]	-0,0107	points
ReCiPe Endpoint (I,A), resources, fossil depletion[RER]	-4,15	points
ReCiPe Endpoint (I,A), resources, total[RER]	-4,16	points
ReCiPe Endpoint (I,A), ecosystem quality, agricultural land occupation[RER]	-0,0588	points
ReCiPe Endpoint (I,A), ecosystem quality, natural land transformation[RER]	-0,0555	points
ReCiPe Endpoint (I,A), ecosystem quality, freshwater eutrophication[RER]	0,0184	points
ReCiPe Endpoint (I,A), ecosystem quality, marine ecotoxicity[RER]	2,41E-06	points
ReCiPe Endpoint (I,A), ecosystem quality, terrestrial acidification[RER]	0,00212	points
ReCiPe Endpoint (I,A), ecosystem quality, terrestrial ecotoxicity[RER]	0,0888	points
ReCiPe Endpoint (I,A), ecosystem quality, climate change, ecosystems[RER]	2,54	points
ReCiPe Endpoint (I,A), ecosystem quality, total[RER]	2,51	points
ReCiPe Endpoint (I,A), ecosystem quality, freshwater ecotoxicity[RER]	0,000605	points
ReCiPe Endpoint (I,A), ecosystem quality, urban land occupation[RER]	-0,0228	points
ReCiPe Endpoint (I,A), total, total[RER]	2,9	points

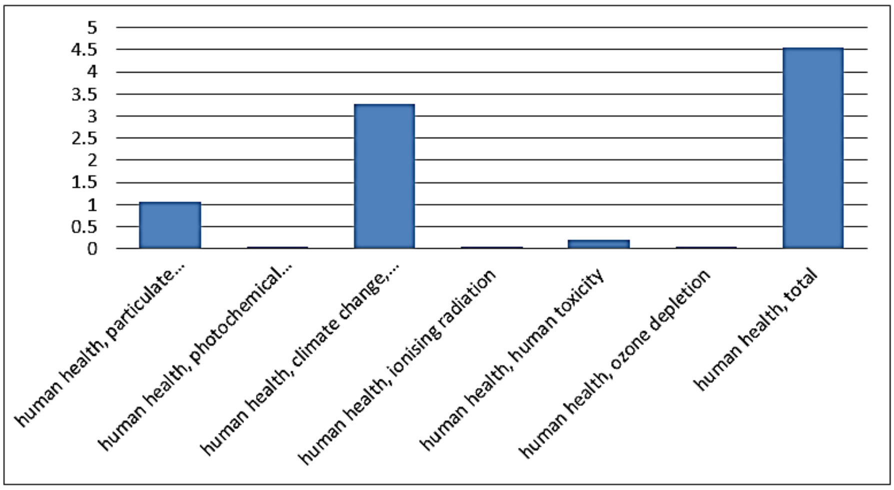

Figure 1. Damage to Human Health, ReCiPe Method

Environmental impact assessment (LCIA)

In life-cycle impact assessment (LCIA), the life-cycle inventory data, which represent all emissions released by the product system to the environment and all raw material requirements, are converted into environmental impact categories. The results are generally referred to as LCA end-point results. In this study, the software used is CMLCA of CML Leiden and ECOINVENT database. The ReCiPe Endpoint method is used to calculate environmental impacts.

RESULTS AND DISCUSSIONS

Table 1 shows the results of environmental impacts calculated using the ReCiPe method, in ecopints. The ecopoint represents one-millimeter of the annual environmental load of an average European inhabitant. This measure thus expresses environmental damage, so higher values are more impacted. I risultati, sono stati raggruppati in tre categorie di danno ambientale: Human Health, Ecoyistem Quality, Resources depletion. The graph in Figure 1 reports the damage to human health. Life cycle assessments commonly assess damage to human health using the concept of 'disability-adjusted life years' (DALY). Values for disability-adjusted life years have been reported for a wide range of diseases, including various cancer types, vector-borne diseases and no communicable diseases. In ReCiPe, we apply the DALY concept, including years of life lost and years of life disabled, without age weighting and discounting, as a default setting for quantifying the damage contributing to the human health area of protection within LCA. In this case, human health is damaged by the impact of global warming (72%) and later on by the formation of particulate matter (23%). The risk that humanity will run out of resources for future generations is often quoted as an important issue. Some groups consider resource depletion as the only issue to be monitored. the ReCiPe model is built on the geological distribution of mineral and fossil resources and assess how the use of these resources causes marginal changes in the efforts to extract future resources. In terms of minerals, the effect of extraction is that the average grade of the ore declines, while for fossil resources, the effect is that not only conventional fossil fuels but also less conventional fuels need to be exploited, as the conventional fossil fuels cannot cope with the increasing demand. In this study, the graph in Figure 2 shows that fossil fuels are the most exploited re source, they are 99,76% of the total.

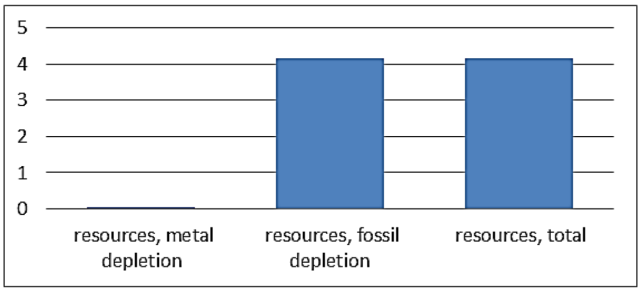

Figure 2. Damage to Resources Depletion, ReCiPe Method

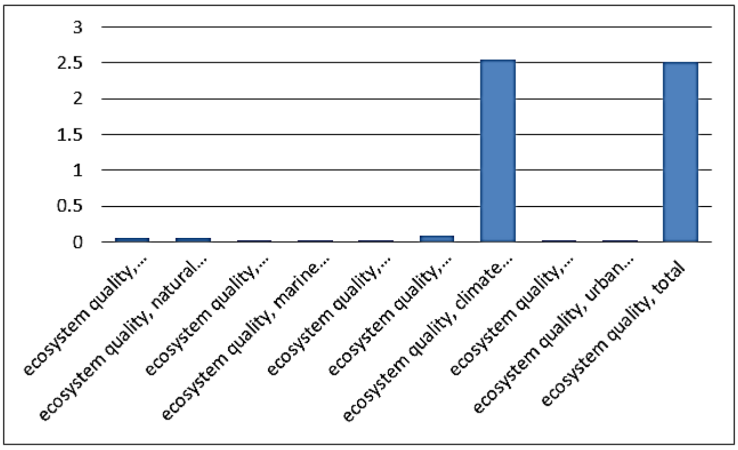

Figure 3. Damage to Ecosystem Quality, ReCiPe Method

Finally, the figure 3 shows, the damage on the ecosystem quality. Ecosystems are heterogeneous and very complex to monitor. A number of treaties, decrees and nonbinding agreements (UNCED, UNEP, Council of Europe) have been drawn up that list those attributes considered to be important to mankind on a whole, such as biodiversity, aesthetic and cultural values, ecological functions and services, ecological resources and information functions. One approach to describing ecosystem quality is in terms of energy, matter and information flows. When such flows are used to characterize ecosystem quality, it can be said that a high ecosystem quality is the condition that allows flows to occur without noticeable disruption by anthropogenic activities. In contrast, a low eco system quality is the condition in which these flows are disrupted by anthropogenic activities. Consequently, it is the level of the disruption that is the most important parameter when ecosystem quality is being measured. As can be seen from the graph, Figure 3, the greatest damage to the ecosystem is due to global warming, and this also confirms the results obtained previously on other categories of environmental damage. In conclusion, the chemical products used in the cryogenic process (chemical treatment), analyzed to recycle photovoltaic panels is the critical point that creates the greatest damage to the environment.

CONCLUSION

The product under consideration usually goes to landfill or alternatively undergoes an incineration and recovery process without any prior treatment. This creates the next dispersion in the environment of highly polluting substances. Using processes to recycle such products, it is possible protect the environment and human health and, another advantage of recycling may be the recovery of materials that in many cases have a high economic value. At this point it's important to understand the impact of processes used to recycle the materials retrieved from the photovoltaic panel. This study analyzes the cryogenic process by applying the LCA method. A series of environmental indicators are computed, and the results show that the critical point is the use of the chemical products, in the chemical treatment. These products are in fact derived from non-renewable fossil fuels, which in turn create greenhouse gas emissions. An improvement in the process could therefore be the use of a different treatment, or replace or diminish the use of chemical products.

REFERENCES

1. Dassisti, M., 2013, Thermo-mechanical controlled cryogenic delamination process for the full recovery of rigid mono- polycrystalline or amorphous materials coated with plastic materials, Patent no. PCT/IT2013/000135 (WO2014141311).
2. Frankl, P., E., Menichetti, M., Raugei, S., Lombardelli, S., Prennushi, G., 2005, *Final report on technical data, costs and life cycle inventories of PV applications,* Deliverable no. 11.2-RS Ia of the NEEDS (New Energy Externalities Developments for Sustainability) project, Rome , Italy .
3. Fraunhofer Institut fur Bauphysik, 2012, Life Cycle Assessment(LCA) screening of the Maltha recycling process for Si-PV modules, Executive summary
4. Frisson, L., Lieten, k., Bruton, T., Declerocq, K., Szlufcik J., 200), Recent improvements in industrial improvement in industrial PV module recycling, 16th European Photovoltaic Solar Energy Conference, Glasgow, UK.

5. Klugmann Radziemska , E., Ostrowski, P.,2010, Chemical treatment of crystalline silicon solar cells as a method of recovering pure silicon from photovoltaic modules, renewable energy, Volume 35, Issue8, Pages 1751–1759.
6. ISO (2006a), *ISO 14040 International Standard. In: Environmental Management – Life Cycle Assessment – Principles and Framework.* International Organisation for Standardization, Geneva, Switzerland.ISO,
7. ISO (2006b), *ISO 14044 International Standard. In: Environmental Management – Life Cycle Assessment – Requirements and Guidelines.* International Organisation for Standardisation, Geneva, Switzerland
8. Muller, A., Wambach,K., Alsema, E., 2005, Life cycle analysis of solar module recycling process, in:Proceedings of the 20th European Photovoltaic Solar Energy Conference, Barcelona, Spain, 6 -10 June.
9. Held, M., Ilg, R., 2011, Uptade of environmental indicators and energy payback time of CdTe PV systems in Europe, Progress in Photovoltaics, Vol.18, N 5, Pages 614-626.

COOL ROOFS IN SUSTAINABLE CIVIL ENGINEERING

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ABSTRACT

The urban heat island effects can be detected throughout the year, but they are of particular importance for the health of human population during summer when air temperatures are high. These heat islands cause increased electricity demand for air conditioning, as well as air pollution which increases with the increase of environment temperature.

Mitigation of the urban heat island effect, among other methods, can be accomplished through the use of Cool Roofs. A cool roof is one that reflects the sun’s heat and emits absorbed radiation back into the atmosphere at a higher rate than standard materials. These types of roofs literally stay cooler, thus reducing the amount of heat held and transferred to the building below. In this way the building remains cooler and at a more constant temperature. The paper presents the properties and types of cool roofs and the advantages of their usage in urban environments.

Key words: cool roofs, solar reflectance (SR), thermal emittance (TE).

INTRODUCTION

According to the Intergovernmental Panel on Climate Change, the Earth’s average temperature is on track to increase by between 2 and 7 degrees Celsius this century. This dramatic change in temperature will produce a climate unfavorable for human population . Cities are often significantly warmer than the surrounding landscapes because urban surfaces absorb more sunlight than natural landscapes, cities lack vegetation, which cools landscapes by evaporating water, and urban areas release more heat from human activity.

The difference between air temperatures in a city and its surrounding rural areas can be 5 to 9 degrees Celsius or more in summer months [1,2]. This phenomenon gave rise to the term - the urban heat island effect (UHI). The urban heat island effect can be observed throughout the year, but it is specially prominent during summer.

It should be mentioned that the temperature difference is usually larger at night than during the day, and is most apparent when winds are weak because the warm air cannot be removed and in addition the surfaces which make up the structures emit at night the thermal energy absorbed by day. All the mentioned factors increase the health problems due to thermal stress, and somtimes lead to fatal outcomes.

As such, urban heat island effect is a serous problem faced by the built up urban areas [3].

Addressing this heating effect will become more important because the world is rapidly urbanizing—within 50 years an estimated 80 percent of the world's population will live in an urban area [1,4] Studies of a city's "urban fabric" indicate that about 60 percent of urban surfaces are covered by roofs or pavements. About 20 to 25 percent are roofs and 30 to 45 percent are pavements [5]. These surfaces are dark and typically absorb over 80 percent of sunlight and in this way heat up the surrounding air. The effects of roofs on warming the environment can be mitigated by using cold material, the so called cold roofs. They feature high solar reflectance and infrared emittance values [1].

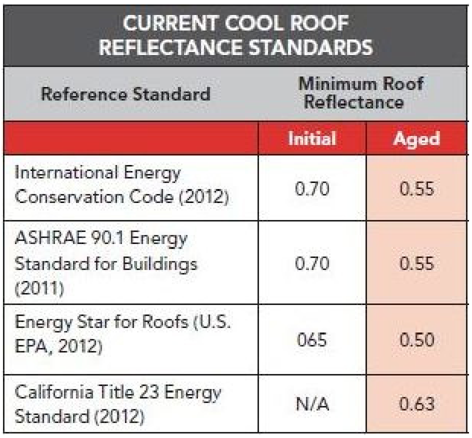
Cool roofs paired with appropriate levels of roof insulation help keep buildings more thermally comfortable.

Cool roofs and pavements should be a priority strategy because they are cost-effective and typically pay back within one year. This is the most acceptable way of helping cities both mitigate the climate change while making them more desirable and comfortable places to live.

COOL ROOFS

Cool roofs are roofs made of high reflectance and emittance materials which can be cooler for 28-33°C during the hottest summer days than the traditional roofs [6]. Reflecting the sun's energy to keep cool is an ancient strategy that has been made modern with science and innovation. Cool roofs have been widely available in the U.S. marketplace for more than 25 years.

For any of these roofing products to be "cool" by today's standards, the minimum percentage of solar heat reflected away from the building typically falls within a range of 0.50 (50 percent) to 0.70 (70 percent depending on the particular standard being applied and the aging of the sample tested. The table 1 shows the building codes and standards used for cool roofs [5].



CURRENT COOL ROOF REFLECTANCE STANDARDS

Reference Standard	Minimum Roof Reflectance	
	Initial	Aged
International Energy Conservation Code (2012)	0.70	0.55
ASHRAE 90.1 Energy Standard for Buildings (2011)	0.70	0.55
Energy Star for Roofs (U.S. EPA, 2012)	065	0.50
California Title 23 Energy Standard (2012)	N/A	0.63

Table 1. Current cool roof reflectance standards [5].

The two radiative properties that characterize cool roofs are solar reflectance and thermal emittance, Figure 1. A cool roof minimizes the solar heat gain of a building by first reflecting incoming radiation and then by quickly re-emitting the remaining absorbed portion. As a result, the cool roof stays cooler than a traditional roof of similar construction.

Solar Reflectance is the fraction of sunlight that a surface reflects. Solar radiation consists of three forms of energy: around 5% of ultra violet light, 45% of visible light and 50% of infrared light. Sunlight that is not reflected is absorbed as heat.

Solar reflectance is measured on a scale of 0 to 1. For example, a surface that reflects 55% of sunlight has a solar reflectance of 0.55. Most dark roof materials reflect 5 to 20% of incoming sunlight, while light-colored roof materials typically reflect 55 to 90%. Solar reflectance has the biggest effect on keeping your roof cool in the sun [6].

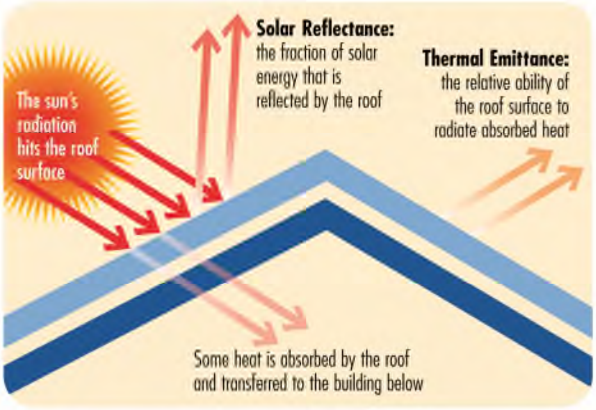


Figure 1. Typical dark roofs absorb 90% and more of solar energy, and white cool roofs can absorb less than 50% of sunlight [6].

Thermal Emittance describes how efficiently a surface cools itself by emitting thermal radiation. Thermal emittance is measured on a scale of 0 to 1, where a value of 1 indicates a perfectly efficient emitter. Nearly all nonmetallic surfaces, have high thermal emittance, usually between 0.80 and 0.95, that helps them cool down.

Bare, shiny metal surfaces, like aluminum foil, have low thermal emittance, which helps them stay warm. A bare metal surface that reflects as much sunlight as a white surface will stay warmer in the sun because it emits less thermal radiation [6].

Though most roofing materials have a fairly high thermal emittance, in order to accurately determine a roofing product's "coolness," or its ability to shield the building beneath it from heat, both solar reflectance and thermal emittance must be measured. It is possible for a roofing product to have a very high emittance value and a reflectance value ranging from very high to very low, or vice versa, which leads to the conclusion that such products would not typically be considered "cool" roofs [7].

Solar Reflectance Index (SRI) – Codes and standards that specify cool roofing requirements may also reference an additional calculated value, the Solar Reflectance

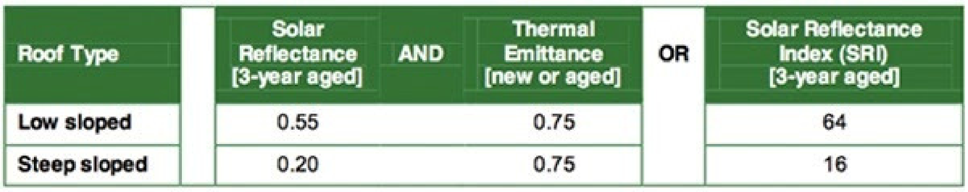
Index (SRI). SRI allows actual measured solar reflectance and thermal emittance values to be combined into a single value by determining how hot a surface would get relative to standard black and standard white surfaces. The standard black roofing material has a high emittance value (90 percent) but a low reflectance value (5 percent). This creates a hot roof surface because even though the emittance is high, there is not enough reflectance to help cool the roof. As such, the standard black roof is given an SRI value of 0.

The standard white roofing material is highly reflective (80 percent) and has the same emittance as the standard black surface (90 percent). Its surface is much cooler and the standard white roof is assigned an SRI value of 100. Like solar reflectance and thermal emittance, a higher SRI value is synonymous with a cooler roof [7].

COOL ROOF QUALITY REQUIREMENTS

Typical minimum cool roof requirements are shown in Table 2. A roof can qualify as cool in one of two ways. The first way is by meeting the minimum solar reflectance and thermal emittance values provided in the table. The alternative way is to meet the minimum SRI requirement. This allows some roofs that have a low thermal emittance and a high solar reflectance (or vice versa) to still qualify as a cool roof.

Table 2. Typical Minimum Cool Roof Requirements, California Energy Commission [8].

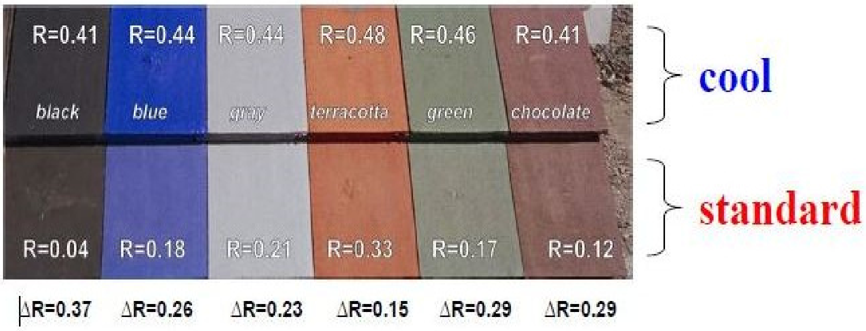


Roof Type		Solar Reflectance [3-year aged]	AND	Thermal Emittance [new or aged]	OR	Solar Reflectance Index (SRI) [3-year aged]
Low sloped		0.55		0.75		64
Steep sloped		0.20		0.75		16

NOT ALL COOL ROOFS ARE WHITE

It is known that white materials tend to be very good solar reflectors. However, colored roofing materials can also be made to reflect more sunlight, Figure 2.

More than half of the sunlight heating the roofs is in the spectrum invisible to the human eye, - infrared and ultraviolet (which does not affect the color of the objects). A colored surface that reflects much of the invisible sunlight is a called a *cool dark color*, or *cool color*. A cool dark color reflects more sunlight than a similar-looking conventional dark color, but less than a light-colored surface. For example, a conventional dark colored surface might reflect 20% of incoming sunlight, a cool dark colored surface, 40%; and a light-colored surface, 80% [6].



Courtesy
American
Rooftile
Coatings

Figure 2. Cool Dark Colors, Cool-colored tiles (top row) look just like conventionally colored tiles but have higher solar reflectance (R) [9].

PRODUCT TYPES

Materials for roofs can vary from asphalt to acrylics, and many of these products have cool roof alternatives. The following list provides examples of some common roofing product types, but does not account for every single type of roofing material in the market:

Built-up Roofing **(includes asphalt and coal tar pitch):** Built-up Roofing (BUR) consists of built-up layers of coated asphalt and insulation applied on site and can be covered with a capsheet or field-applied coating. The "cool" part of this particular roof type refers to the properties of the capsheet, typically a white mineral fiberglass surface, or coating, which are UV-resistant.

Foam Roof Systems:

a) Field-applied foam systems are sprayed on in liquid form and harden as they set on top of the roof.

b) Factory-applied foam systems are formed into rigid panels and coated with a reflective coating in the factory. The foam usually gives the roof system additional insulation properties and the coatings provide the "cool" rating.

Metal - Metal roofing products can be shaped to look like shingles or shakes, or to fit unique curvatures, in addition to a typical standing seam configuration. They come in a variety of factory-applied textures and colors, including darker "cool" colors with infrared reflective pigments. Metal products can also be coated in "cool" custom colors to meet the cool roof conditions..

Modified Bitumen - Modified bitumen is bitumen (asphalt or tar) modified with plastic and layered with reinforcing materials then topped with a surfacing material. Like BURs, the radiative properties of modified bitumen are determined by the surfacing material, so a "cool" modified bitumen product will be finished off with a capsheet or coating to achieve a high solar reflectance.

Roof Coatings - Roof coatings can be divided into two categories: **field-applied** and **factory-applied.** Field-applied coatings are applied directly onto the roof surface, either on a new roof assembly or over an existing roof surface and may require an appropriate primer. Factory-applied coatings are applied directly to products at the factory. Examples of factory-applied coatings include coatings applied to metal, and glazes that are applied to tiles. Once applied, the coating is what determines the reflective properties of the roofing product.

Shingles, Slate, or Tile: These roofing products are commonly used for residential buildings, or steeper-sloped buildings, and rarely for public buildings. For "cool" colored shingles, the heightened solar reflectance comes from granules that contain solar-reflective pigments. Slate and tile products have solar-reflective surfaces in a number colors. The earthen composition of slate and tile products provides increased thermal mass, which has detrimental effects on thermal emittance.

Single-ply: Single-ply roofing is a pre-fabricated sheet of rubber polymers. The single-ply membrane can be loose-laid and weighted down with ballast or pavers or firmly set on the roof and attached with mechanical fasteners or adhesives. There are two main types of single-ply materials: **single-ply thermoset** and **single-ply thermoplastic**. These roofing products can be specified with an ultra-violet-resistant and highly reflective surface [7] .

BENEFITS OF COOL ROOFS

Cool roofs may be made from a wide variety of materials, such as: metal, modified bitumen, slates, paints, roof tiles, coatings, shingles and rubber polymers. They can be installed on flat and sloped roofs, on commercial and residential buildings, in new construction and on existing structures. Although many cool roofs are light-colored or white, they are increasingly being created in a range of colors and can look nearly identical to traditional roofing materials. A cool roof can be 28 to 33°C cooler than a dark, conventional roof on a hot summer day. Cool roofs help reduce energy use and GHG emissions, save money on air-conditioning costs, and improve air quality. When enough are installed on a citywide scale, cool roofs can also reduce the urban heat island effect—helping to lower temperatures across whole urban communities [10].

CONCLUSION

A cool roof is one that strongly reflects sunlight and also cools itself by efficiently emitting radiation to its surroundings. However, a cool roof need not be white. There are many "cool color" products which use darker-colored pigments that are highly reflective in the near infrared (non-visible) portion of the solar spectrum. Because a white roof strongly reflects both visible and near infrared sunlight, a white roof will typically be cooler than a cool colored roof. The two basic characteristics that determine the "coolness" of a roof are solar reflectance (SR) and thermal emittance (TE). Both properties are rated on a scale from 0 to 1, where 1 is the most reflective or emissive. A cool roof can significantly reduce the cooling energy costs and increase the comfort level by reducing temperature fluctuations inside building. Average energy savings range from 7%-15% of total cooling costs [11].

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REFERENCES

1. A Practical Guide to Cool Roofs and Cool Pavements, Global Cool Cities Alliance (GCCA), coo R20 Regions of Climate Action, January 2012
2. Remote sensing of the urban heat island effect across biomes in the continental USA. Remote Sensing of the Environment, 114 504-513
3. Cool Roofs: City of Melbourne Research Report, September 2011,The University of Melbourne
4. Crutzen, P. J. (2004). New directions: The growing urban heat and pollution "island" effect – impact on chemistry and climate. *Atmospheric Environment, 38*(21), 3539-3540.
5. Cool Roofs for a Hot Planet, Sponsored by Duro-Last, Inc. Education - Advertisement
6. Guidelines for Selecting Cool Roofs, July 2010 V. 1.2, Prepared by the Fraunhofer Center for Sustainable Energy Systems for the U.S. Department of Energy Building Technologies Program and Oak Ridge National Laboratory under contract DE-AC05-00OR22725.
   Additional technical support provided by Lawrence Berkeley National Laboratory and the Federal Energy Management Program. Authors: Bryan Urban and Kurt Roth, Ph.D.
7. What's So Cool About Cool Roofs?, Reprinted from GreenSource, March/April 2009, Advertising Supplement Provided by Cool Roof Rating Council
8. California Energy Commission. 2008. "2008 Building energy efficiency standards for residential and nonresidential buildings." December
9. https://energy.gov/sites/prod/files/2015/07/f25/Cool_Roofing_Technologies.pdf
10. Noah Garrison - Natural Resources Defense Council, Cara Horowitz - Emmett Center on Climate Change and the Environment at UCLA, School of Law, „Looking Up: How Green Roofs and Cool Roofsm Can Reduce Energy Use", Address Climate Change, and Protect Water Resources in Southern California, NRDC Report, june 2012 r:12-06-B
11. http://coolroofs.org/resources/home-building-owners.

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RELIABILITY OFANALYTICAL DATA FOR THE RISK ASSESSMENT OF ABANDONED MINE ENVIRONMENT

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ABSTRACT

Mining activities may affect ecosystems and cause environmental pollution. So, reliable analytical results are necessary in order to assess environmental impact of mining activities. In this study, tungsten mine wastes were assessed with soil-rainwater interactions by focusing the validated metal analysis. In this context, sample preparation strategies were overviewed for the determination of tungsten. Chemometric techniques were applied to soil samples in order to shorten the analysis time as an example. Rainwater samples were also given for copper analysis using hyphenated techniques. The qualities of the results were evaluated in terms of analytical priority.

Key words: tungsten, copper, soil, rainwater, method validation, inductively coupled plasma-mass spectrometry.

INTRODUCTION

Soils have complex matrix contents originating from organic or inorganic materials and metal compounds from mainly anthropogenic sources that necessitate chemical dissolution prior to some of the atomic spectrometric techniques such as inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) [1]. Trace metal content in this matrix depends on geochemical factors, the nature of the material and formation processes [2]. So, specific soil profiles may be different in terms of texture, structure, organic content, pH, bulk density, drainage, water holding capacity, fertility [1] that lead ecological diversity for sample preparation strategies. So, elemental determinations in soils are challenging and alternative or complementary strategies come to the forefront [3-5]. As an example, Hassan et al. [6], used modified EPA Method 3051 to improve the recoveries for many elements in soil samples by hydrochloric acid addition, although the digestion did not result any important improvement in the recovery for most of the studied elements and they mentioned the interferences originating from the chloride in the matrix [1, 6].

Mining activities may cause pollution in the environment that result in elevated metal concentrations in soil and water due to the dispersion and discharge of mine waste. Thus, these may threat the natural ecosystems through decreased biodiversity, simplified structure, and lowered productivity and human health via the food web [7, 8]. So, reliable analytical results are necessary in order to assess environmental impact of mining activities.

For elemental analysis of many environmental soil and sediment matrices partial or total chemical dissolution prior to analysis is one of the mandatory steps [3]. On the other hand, the inherent heterogeneity of the matrices originating from the sample structures lead analytical complexity for the analysis [1, 3, 4] and the determination of some elements in soil, plant and water matrices are challenging.

Beyond the other elements in soil samples, tungsten (W) is an important metal with many industrial, household, scientific and military applications [9, 10]. It occurs in small concentrations naturally in soils and sediments, although many anthropogenic or industrial activities may significantly increase its concentration in environment [9]. Environmental effects of W and its physiological similarities, chemical relations/competitions with some elements such as molybdenum and vanadium addressed in many papers [9-11]. Nevertheless, the biochemical effects of tungsten compounds are not well identified [9]. In addition, regulation of tungsten, in terms of environmental and occupational safety is limited compared with other metals [12] and potential toxicity of soluble tungsten is mentioned [13]. So, it is stated that historical knowledge of tungsten with ''nontoxic'' or ''environmentally inert'' characteristics have to be re-evaluated and environmental regulations are needed as a result of this attempts [11].

In the literature, it is outlined that traditional acid digestion procedures for elemental W analysis are insufficient for leaching because of the precipitated insoluble tungstic acid and polytungstic acids [14]. Some strong extraction procedures have been modified and used to improve the recovery of W from soil. Nevertheless, existing methodological approaches mostly seems time-consuming and variable recovery values could be found derived from the nature of soil and its components [4]. Although a certified reference material or recovery studies were used for method validation, it will depend on the similarity of W form in the samples, added standards or the certified materials [4, 14] that may define the needed of total dissolution methods or not for analysis purposes.

The study of trace metals in wet/dry precipitation has also increased in the last decades depending on their apparent environmental and human health effects. Metals from precipitates may also accumulate in soils, surface waters, etc. that lead adverse effects to aquatic life and forest ecosystems [15]. Lee et al., studied mineralogical aspects of secondary minerals and natural removal process of dissolved As from waste rock materials and contaminated soils as well as the effects of acid rainwater or acid mine drainage [16]. Petrunic and Al, also studied the pore-water geochemistry and mineralogy of tailings originated from a granitic tungsten deposit for the analysis of major and minor elemental levels [17]. Thus, the importance of W mine for water resources could be one of the important points of view and may be an indicator of pollution in terms of some atmospheric cations being found in natural rain water. Thus, the aim of this work is to evaluate the W analysis procedures by atomic spectrometry techniques for soil samples in terms of sample preparation methodologies and extend the approach to rain water samples to study the W and copper (Cu) relations originating from soil and rainwater samples, respectively. Inductively coupled plasma-mass spectrometry (ICP-MS) and high performance liquid chromatography (HPLC) coupled online with the ICP-MS were used for this purposes.

MATERIAL AND METHOD

Soil samples of *Anthemis cretica* L. was taken from the waste removal pools around the abandoned Etibank Tungsten Mine Work at Uludağ Mountain, Bursa, Turkey (n=5). This mine area is located at an altitude between 2100 and 2487 m, lying at the intersection of 40° N. latitude and 29° E longitude in a national park [4]. Homogenized and sieved (0.5 mm) soil samples were used for optimization studies. For comparison, a total of 0.5 g of samples were digested according to the method of Bednar et al., which needed approximately six hours of sample preparation periods [14]. Depending on the solvents used in the literature [14, 18, 19] and initial fractionation studies [4] digestion procedure was optimized using central composite design. For this purpose 0.2000 ± 0.0010-g soil samples were digested using Kjeldahl system with different molarities of phosphoric acid, hydrochloric acid, as well as different time and temperature conditions. A total of 30 experiments with all possible experimental conditions were applied derived from the Design Expert (version 7.0.0, STAT-EASE Inc., Minneapolis, USA). Model accuracy and interactive parameters were evaluated according to ANOVA results and three-dimensional response surface plots. Detailed sample preparation was described elsewhere [4]. Four different isotopes of W were analyzed but the most abundant one, W-184 isotope was used. Method validation parameters are outlined in our earlier study [4]. Rainwater samples were collected triplicate from the same area at different times in the same season of February-March through the Bursa city center-Osmangazi/Bursa-Turkey which is in sufficient distance from industrial area ($n=3$) [20, 21]. 4 mL of rainwater samples were digested with 2 mL of nitric acid and 1 mL of hydrogen peroxide then diluted to 25 mL for total element determinations using digestion. Particulate Cu (difference between unfiltered/digested and 0.2 µm-filtered samples), colloidal Cu (from the difference between the 0.2 µm-filtered and 0.45 µm-filtered samples), and dissolved Cu (from the samples which passed through the 0.22 µm filter) were analyzed directly by ICP-MS. Also, 0.45 µm-filtered samples were analyzed by ICP-MS (total Cu without digestion) and by on-line HPLC-ICP-MS system. Cu concentrations based on the peak heights of external calibration were evaluated instead of peak area to eliminate possible interferences. The calibration details were outlined by Erdemir [20].

Tungsten/copper levels in the samples were determined by an Elan 9000 ICP-MS (PerkinElmer Sciex, Shelton, CT, USA) and high performance liquid chromatography (HPLC) coupled online with the ICP-MS instrument through a Rheodyne switching valve apparatus (with 6 port, 2 position, PerkinElmer Sciex) using high-purity fluoropolymer tubing (PFA, Poly Fluorinated Alkoxy, 0.019 in. i.d., 1/16 in. o.d., and 580 mm length, PerkinElmer Sciex). The components/operating conditions of HPLC-ICP-MS were as follows: PerkinElmer 200 series high-performance liquid chromatograph, a series 200 quaternary pump, a series 225 autosampler, a series 200 column oven, and a vacuum degasser; software package, Chromera (version 1.2.254.0, PerkinElmer SCIEX) Analytical column, Brownlee DB Aq. C-18 (150 mm×4.6 mm i.d., 5 mm, PerkinElmer SCIEX); column temperature, 26°C; mobile phase, water; elution, isocratic-1.5 mL min^{-1}; analysis time, 10 min; injection volume, 30µL [20]. Additionally, the components/operating conditions of the ICP-MS equipment were: PerkinElmer Ryton cross-flow nebulizer, a Scott-type double-pass spray chamber, a standard glass torch, nickel sampler, and skimmer cones (i.d.: 1.1 mm and 0.9 mm, respectively). RF power, 1000 W; plasma argon flow rate, 17.0 L min^{-1} ; auxiliary argon flow rate, 1.2 L min^{-1} ; nebulizer flow rate, 0.85 L min^{-1} ; sample uptake rate, 1.5 mL min^{-1} [4].

RESULTS AND DISCUSSION

Numerous papers have published related the abandoned W mine work by our research group with different plant species and their soils [7, 22, 23] which uses existing methodological approach proposed by Bednar et al. [14]. Apart from these studies, Erdemir [4] showed the versatility of central composite design as an effective tool for optimizing the analytical procedure with desired extractability of W. This optimized digestion method could be used as a fast and efficient alternative to the one of the earlier proposed method [14] as the two methods were compared in details [4, 14]. Reliability of the data was evaluated by multi directional approach as detailed by Erdemir and concluded the optimum conditions of 9 M H_3PO_4, 124℃ digestion temperature, 45 min digestion time and 1.52 M HCl for efficient extraction of W from soil samples [4]. In addition to achieved short-time efficient sample preparation step, as the W content of soils as well as transported elements by air could be indicators of accumulation/pollution/synergism behaviors of elements in the ecosystem of the abandoned mine area, achieved results could be compared and explained with selected elemental levels of the rainwater samples to specify the transportation characteristics. Total (without digestion), colloidal, particulate and dissolved Cu levels of the rainwater samples were in the range of 2.7-4.8, 0.3-1.7, 0.2-3.3, 3.3-4.6 µg L^{-1} levels, respectively. Achieved under detection levels of Cu after hyphenated analysis, shows the tendency of particulate form of Cu in rainwater samples for wet deposition. These small Cu levels also indicates that copper could not transported by rainwater. As the achieved/found results represent the studies from 2002 to 2016, it is found that Cu contents of the same samples were decreased in the same area and for the same species from 2002 to 2016 [7, 24], the results may show the soluble character of Cu from surface soil compartments to inter layer and indicates the possibility of further contamination of ground water by rainwater.

CONCLUSION

As W content of abandoned mine area could be important to indicate the accumulation in plant species and/or to reflect important milestone in phytoremediation-based works, reliable and validated sample preparation strategies were have to be taken into account. This study shows the practical characteristic of one of the response surface methodology for optimizing the digestion procedures using a four-factor and five-level central composite design. Validated data assessment presents the utility and the efficiency of the developed method against known sample preparation pathways before. Additionally, rainwater analyses were used to identify the transportation characteristics of Cu through air and the possible relations could be evaluated between W and Cu analysis based on the obtained data assessment.

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REFERENCES

1. Akbulut, S., Cevik, U., Van, A.A., De Wael, K., Van Grieken, R. (2014). Precision and accuracy of ST-EDXRF performance for As determination comparing with ICP-MS and evaluation of As deviation in the soil media. Chemosphere, 96, 16–22.
2. Roje, V. (2010). A fast method for multi-metal determination in soil samples by high-resolution inductively-coupled plasma-mass spectrometry (HR–ICP–MS). Chemical Speciation and Bioavailability, 22, 135–139.
3. Voica, C., Dehelean, A., Iordache, A., Geana, I. (2012). Method validation for determination of metals in soils by ICP-MS. Romanian Reports in Physics, 64, 221–231.
4. Seven Erdemir U. (2016). Development of sample preparation strategy for the determination of tungsten in soil samples by inductively coupled plasma-mass spectrometry using a response surface methodology. Turkish Journal of Chemistry, in press, DOI: 10.3906/kim-1607-19.
5. Alothman, Z. A., Yılmaz, E., Habila, M., Soylak, M. (2015). Separation and preconcentration of lead(II), cobalt(II), and nickel(II) on EDTA immobilized activated carbon cloth prior to flame atomic absorption spectrometric determination in environmental samples. Turkish Journal of Chemistry, 39, 1038–1049.
6. Hassan, N.M., Rasmussen, P.E., Dabek-Zlotorzynska, E., Celo, V., Chen, H. (2007). Analysis of environmental samples using microwave-assisted acid digestion and inductively coupled plasma mass spectrometry: maximizing total element recoveries. Water Air and Soil Pollution, 178, 323–334.
7. Guleryuz, G., Erdemir, U.S., Arslan, H., Gucer, S. (2016). Elemental composition of Marrubium astracanicum Jacq. growing in tungsten-contaminated sites. Environmental Science and Pollution Research, 23, 18332–18342.

8. Koz, B. (2014). Energy-dispersive X-ray fluorescence analysis of moss and soil from abandoned mining of Pb-Zn ores. Environmental Monitoring and Assessment, 186, 5315–5326.
9. Strigul, N., Koutsospyros, A., Arienti, P., Christodoulatos, C., Dermatas, D., Braida, W. (2005). Effects of tungsten on environmental systems. Chemosphere, 61, 248–258.
10. Adamakis, I.-D. S., Panteris, E., Eleftheriou, E.P. (2010). Tungsten affects the cortical microtubules of Pisum sativum root cells: experiments on tungsten–molybdenum antagonism. Plant Biology, 12, 114–124.
11. Strigul, N. (2010). Does speciation matter for tungsten ecotoxicology?. Ecotoxicology and Environmental Safety, 73, 1099–1113.
12. Koutsospyros, A., Braida, W., Christodoulatos, C., Dermatas, D., Strigul, N. (2006). A review of tungsten: From environmental obscurity to scrutiny. Journal of Hazardous Materials, 136, 1–19.
13. Thomas, V.G., Roberts, M.J., Harrison, P.T.C. (2009). Assessment of the environmental toxicity and carcinogenicity of tungsten-based shot. Ecotoxicology and Environmental Safety, 72, 1031–1037.
14. Bednar, A. J., Jones, W. T., Chappell, M. A., Johnson D. R., Ringelberg, D.B. (2010). A modified acid digestion procedure for extraction of tungsten from soil. Talanta, 80, 1257–1263.
15. Baez, A., Belmont, R., Garcia, R., Padilla, H., Torres, M.C. (2007). Chemical composition of rainwater collected at a southwest site of Mexico City, Mexico. Atmospheric Research, 86, 61 – 75.
16. Lee, P., Kang, M.J., Choi, S.H., Touray, J.C. (2005). Sulfide oxidation and the natural attenuation of arsenic and trace metals in the waste rocks of the abandoned Seobo tungsten mine, Korea. Applied Geochemistry, 20, 1687–1703.
17. Petrunic, B.M., Al, T.A. (2005). Mineral/water interactions in tailings from a tungsten mine, Mount Pleasant, New Brunswick. Geochimica Et Cosmochimica Acta, 69, 2469–2483.
18. Clausen, J.L., Ketterer, M.E., Bednar, A.J., Koenig, M.R. (2010). Challenges and successes in using inductively coupled plasma mass spectrometry for measurements of tungsten in environmental water and soil samples. International Journal of Environmental Analytical Chemistry, 90, 773–783.
19. Gurmen, S., Timur, S., Arslan, C., Duman, I. (1999). Acidic leaching of scheelite concentrate and production of hetero-poly-tungstate salt. Hydrometallurgy, 51, 227–238.
20. Seven Erdemir, U. (2013). Manganese And Copper Speciation/Fractionation Analysis In Food And Rainwater Samples And HPLC-ICP-MS Technique. PhD thesis, The Graduate School of Natural and Applied Sciences of Uludag University, July 10th, 2013.
21. Erdemir, U.S., Gucer, S. (2017). Manganese speciation studies in Rain water: application of high Performance liquid Chromatography-inductively Coupled plasma mass spectrometry. IWA 2nd Regional Symposium on Water,

Wastewater and Environment, proceedings book, pages 121–125, 22-24 March, Çesme-Izmir, Turkey.

22. Erdemir, U.S., Arslan, H., Guleryuz, G., Gucer, S. (2017). Elemental Composition of Plant Species from an Abandoned Tungsten Mining Area: Are They Useful for Biogeochemical Exploration and/or Phytoremediation Purposes?. Bulletin of Environmental Contamination and Toxicology, 98, 299–303.
23. Arslan, H., Erdemir, U.S., Guleryuz, G., Kiazolu, H., Gucer, S. (2017). Assessment of Trace Elements in *Plantago Holosteum* Scop. (Plantaginaceae) from Abandoned Tungsten Mine Work Using Inductively Coupled Plasma Mass Spectrometry. Analytical Letters, in press, DOI: 10.1080/00032719.2017.1308374.
24. Guleryuz, G., Arslan, H., Kirmizi, S., Gucer, S. (2002). Investigation of influence of tungsten mine wastes on the elemental composition of some alpine and subalpine plants on Mount Uludag, Bursa, Turkey. Environmental Pollution, 120, 707–716.

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MORPHOMETRIC CHARACTERISTICS AS INDICATORS OF QUALITY OF ONE-YEAR-OLD SEEDLINGS OF *Juglans nigra L.*

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ABSTRACT

This paper shows the analysis results of morphometric characteristics of black walnut (Juglans nigra L.) one-year-old seedlings, their inter-connection and the relation of morphological indicators of the planting material quality that all have been observed in repetitions in three successive years of research. Except the height and the root collar diameter the following morphometric characteristics have been measured: root length, mass of the aboveground part of plant (shoot) in absolutely dry condition and mass of the underground part of plant (root) in absolutely dry condition. Also, the ratio of diameter and height as well as the quality index of seedlings were calculated.

Key words: black walnut (*Juglans nigra* L.), morphometric characteristics of seedlings, quality index.

INTRODUCTION

The indigenous trees of black walnut on the Balkans can be found in devastated areas and on edge of forests or next to forest roads (Mayer, 2011). The seed falls off the tree, germinates and grows up without any human influence. This shows that the black walnut is very domesticated species in this area and that its natural regeneration is possible and for this reason more attention needs to be given to this species.

The seedling quality is a term that is used to describe the success of survivaland the growth of the seedlings after transplanting (Duryea, 1985; Mattsson,1996). Although the quality of seedlings greatly depends on factors such as plant species, the conditions in which it grows and genetic predisposition it can be defined through the progress of the seedling after transplanting.

According to Stilinović (1960) the basic elements for qualitative classification of seedlings are their height, root collar diameter, mass of the aboveground part, mass of the underground part (the mass can be measured in both fresh and dry condition), length and development of buds, number of buds, structure of root (volume and length), size and density of leaves, the ratio of height and diameter as well as the ratio of the mass of above and underground part of the seedling.

The use of planting material that has poor qualitative characteristics increases the costs for establishing and maintaining of orchards and plant cultures and decreases the afforestation success (Oliet et al., 2009).

To evaluate the seedling quality the morphological indicators such as height and diameter of seedlings have commonly been used (Stilinović, 1960, Mexal and Landis, 1990, Jacobs et al., 2005, Ivetić, 2013). For researches in this paper, except the height and the root collar diameter, the following morphometric characteristics were measured: root length, mass of the aboveground part of plant (shoot) in absolutely dry condition, mass of the underground part of plant (root) in absolutely dry condition; also, the ratio of diameter and height as well as the quality index of seedlings were calculated.

MATERIALS AND METHOD

The trial was set up in three successive years of research (2011, 2012 and 2013) in the nursery of the Institute of forestry in Belgrade, at 20° 27' 44" E longitude and 44° 49' 14"N latitude, at an altitude of 115 meters.

The tree of black walnut from which the fruits were collected and the seed used for sowing and seedling production is located in the Arboretum of the Faculty of forestry in Belgrade at 44° 46' 55" N latitude and 20° 25' 27" E longitude, at an altitude of 120 meters. Due to embryo dormancy the seed was stratified. Stratification lasted from November until the end of March, sand was moist and the temperature was 3-5°C. The sowing was performed in rows at a depth of 8 cm.

The sample consisted of 90 seedlings, 30 seedlings in three replications.

Experimental fields were located on a flat ground in the same conditions of shade cloth and in the same direction of spreading for the reason that for all fields the environmental conditions should be as similar as possible. While the experiment lasted the plants were regularly watered and sprayed three times a week during the dry season with using of shade cloth due to strong insolation and high temperatures.

The following morphometric characteristics were measured: the seedling height (measured with a ruler), the root collar diameter (measured with avernier scale – a nonius), the root length (measured with a ruler of 1 mm accuracy), the mass of the shoot and the root in the absolutely dry condition (after drying at the temperature of 105°C for 48 hours the mass was measured with a digital scale). The ratio of the height and the diameter was calculated (Roller, 1977) as well as the ratio of the mass of the above and underground plant part and Dickson quality index (Dicksonetal., 1960).

The obtained results of the morphological characteristics were processed using appropriate procedures of statistical software package *Statistica 7* – ANOVA, Post hoc Tukey's HSD test, Regression analysis.

RESULTS

Based on analysis of the morphological characteristics in all three years of research their mean values were calculated as well as the basic statistical indicators (Table 1).

Table 1. Basic descriptive statistics indicators for morphometric characteristics of black walnut seedlings

	Mean	**Minimum**	**Maximum**	**Variance**	**Std. dev.**	**Stand. error**
H (cm)	45.9	25.0	69.9	55.52	7.45	0.453
D (mm)	6.43	4.16	10.60	1.21	1.10	0.067
RL (cm)	512	199	900	17,089.09	130.73	7.956
RW (g)	8.10	3.92	13.00	3.37	1.83	0.112
SW (g)	5.13	1.97	9.68	2.27	1.51	0.092
H/D	7.22	4.72	10.56	1.36	1.16	0.071
SW/RW	0.64	0.27	1.02	0.03	0.16	0.010
QI	1.72	0.79	3.15	0.22	0.47	0.028

H – average height, D – diameter, RL – root length, RW – root weight, SW – shoot weight, H/D – height/diameter ratio, SW/RW – shoot weight/root weight ratio, QI – quality index

The mean height for all three years of research is 45.9 cm. The absolutely lowest measured height is 25 cm and the absolutely greatest measured height is 69.9 cm. The mean root collar diameter is 6.43 cm and it ranges from 4.16 to 10.60 mm (amplitude 6.44 mm). The mean ratio H/D is 7.22 and it ranges from 4.72 to 10.56.

The root length varies from 199 to 900 cm in all three years of research. The mean value of this characteristic is 512 cm.

The mass of the underground part of plant in the absolutely dry condition is 8.10 g and it is significantly larger than the average mass of the aboveground part which is 5.13 g. These two characteristics also have a great variability so the root mass ranges from3.92 to 13.00 g and mass of the shoot range from 1.97 to 9.68 g. The ratio of the shoot and the root varies from 0.27 to 1.02 and the average is 0.64.

The mean value of the quality index is 1.72; it ranges from 0.79 to 3.15.

In Tables 2 and 3 are shown the mean values of height and diameter for all three years of research and the mean value for the entire three-year period of experiment repetition.

Table 2. Basic indicators of descriptive statistics for the height of black walnut seedlings in three successive years of research (2011, 2012 and 2013)

Treatment	**Height (mm)**	**Minimum**	**Maximum**	**Variance**	**Std. dev.**	**Stand. error**	**Coefficient of variation**
2011	44.8^{a}	25.0	69.9	96.27	9.81	1.03	21.89
2012	48.4^{b}	37.6	59.0	22.95	4.79	0.50	9.90
2013	44.4^{a}	30.2	59.0	39.08	6.25	0.66	14.07
average	45.9	25.0	69.9	55.52	7.45	0.45	16.23

Mean values in the same column followed by different letters are statistically different for r<0.05 (Post hoc Tukey's HSD test)

Table 3. Basic indicators of descriptive statistics for the root collar diameter of black walnut seedlings in three successive years of research (2011, 2012 and 2013)

Treatment	Diameter (mm)	Minimum	Maximum	Variance	Std. dev.	Stand. error	Coefficient of variation
2011	7.32^b	4.16	10.60	1.90	1.38	0.15	18.85
2012	6.09^a	4.51	7.58	0.34	0.58	0.06	9.52
2013	5.88^a	4.50	6.66	0.19	0.44	0.05	7.48
average	6.43	4.16	10.60	1.21	1.10	0.07	18.71

Mean values in the same column followed by different letters are statistically different for r<0.05 (Post hoc Tukey's HSD test)

Table 4. Correlation of the studied indicators of quality of black walnut one-year-old seedlings

	H (cm)	D (mm)	RL (cm)	RW (g)	SW (g)	H/D	SW/RW	QI
H (cm)	1.00							
D (mm)	0.52**	1.00						
RL (cm)	0.57**	0.48**	1.00					
RW (g)	0.63**	0.55**	0.59**	1.00				
SW (g)	0.46**	0.65**	0.48**	0.56**	1.00			
H/D	0.51**	-0.46**	0.09	0.06	-0.18**	1.00		
SW/RW	-0.05	0.21**	0.02	-0.28**	0.63**	-0.25**	1.00	
QI	0.25**	0.81**	0.44**	0.72**	0.77**	-0.57**	0.20**	1.00

Correlations – Marked correlations are significant at $p < 0.05$ - * and at $p < 0.01$ - ** N=180 (Casewise deletion of missing data)

H – average height, D – diameter, RL – root length, RW – root weight, SW – shoot weight, H/D – height/diameter ratio, SW/RW – shoot weight/root weight ratio, QI – quality index

Having in mind that for measurement of height and root collar diameter is not necessary to "destroy" the plant, these characteristics were brought in correlation with other morphometric characteristics in order to determine which one of these two characteristics can be the representative indicator of the quality of planting material.

The correlation of the height and the diameter of black walnut seedlings (r=0.52) is similar to the correlation obtained by Jacobs et al. (2006).

The combination of independent variables which are the height and the root collar diameter and the dependent variable that is the quality index is shown on the Figure 1. The seedlings with the larger diameter and the smaller height have the higher values of the quality index.

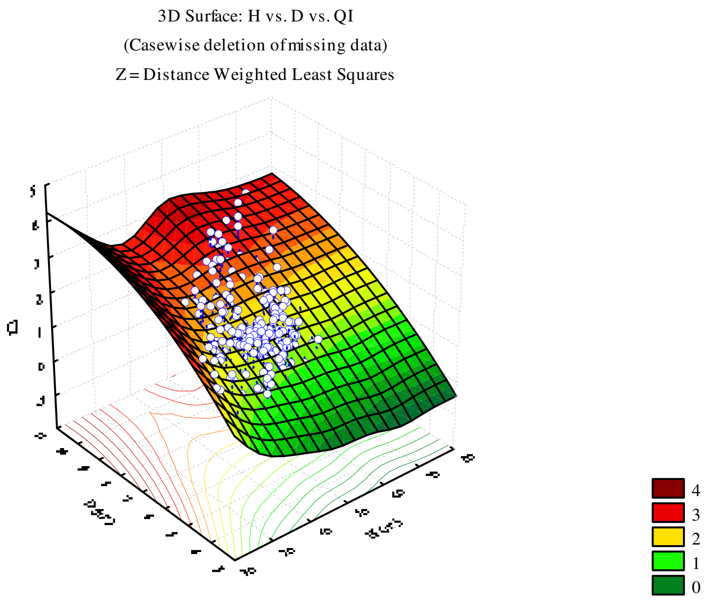

Figure 1. Area of a combination of height (H) and diameter (D) as a predictor as opposed to Quality Index (QI) as the dependent variable

The linear correlation between the quality index and the height of black walnut shoot is weak; the correlation coefficient has a value of 0.25. The value of the correlation coefficient between the quality index and the root collar diameter shows a high level of correlation of these two characteristics, r is 0.81 (Figure 2).

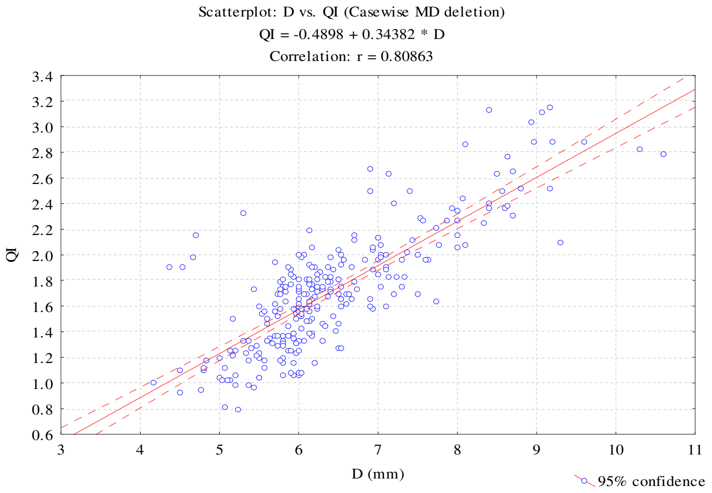

Figure 2. Regression analysis – linear dependence of quality index and root collar diameter

DISCUSSION AND CONCLUSIONS

Since this is the allochthonous species the most important researches for us are those conducted in areas where environmental conditions are similar to that of our region. In their researches on the territory of Serbia, in the vicinity of Kruševac, Krstić and Vojinović (2002) concluded that the average height of one-year-old black walnut seedlings is 39.1 cm, lower than the average height of seedlings in this research. Krstić and Vojinović mention average black walnut root collar diameter of 10.33 mm and it is, unlike the seedling height, greater than the average diameter of the studied plants obtained in all three years of research.

Oršanić et al. (2007) followed the growth and development of black walnut seedlings during the first growing season in a nursery in Zagreb and the measured average height was 31.5 cm at the end of the growing season which is lower than the average height of seedlings in this research. The average root collar diameter of 6.83 mm or 8.03 mm (depending on whether the fruits were cleaned before sowing or not) is similar in size as the average diameters obtained in this research.

Average dimensions of one-year-old black walnut seedlings in this research are comparable with dimensions of black walnut seedlings of the same age at medium sowing density in research of Jacobs et al. (2006).

Woeste et al. (2011) produced seedlings from the seed of the black walnut trees in Indiana (USA), whose average height was 45.6 cm, ranging from 37.4 to 51.3 cm. Also, the research of Woeste et al. (2011) showed that the average root collar diameter of seedlings after the first growing season was 11.5 mm, ranging from 10.6 to 12.2 mm.

The value of the correlation coefficient between the quality index and the root collar diameter shows a high level of correlation. This relation between the diameter and the quality index is expected because the diameter has been reported for several times as the best single morphological indicator of the seedling quality (Mexal and Landis, 1990; Ivetić, 2013, Ćirković-Mitrović et al., 2015). Dickson quality index has also proved to be the most comprehensive indicator of seedling quality in many species (Binotto et al., 2010). The value of the correlation coefficient between the quality index and the mass of shoot and root in absolutely dry condition (0.72 and 0.77) also indicates a very good correlation of these characteristics.

Based on the research results and the analysis of morphometric characteristics of black walnut seedlings, it can be concluded that the height and the root collar diameter are the good indicators of quality, whereby the diameter may be preferable due to a stronger positive correlation with the quality index. Also, to the strong correlation between the quality index and the mass of the shoot in absolute dry condition indicates the high value of the correlation coefficient for these two characteristics.

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REFERENCES

1. Binotto, A. F., Lúcio, A. D. C., Lopes, S. J. 2010. Correlations between growth variables and the Dickson Quality Index in forest seedlings, *Cerne*, Vol. 16(4), 457-464.
2. Dickson, A., Leaf, A. L., Hosner, J. F. 1960. Quality appraisal of white spruce and white pine seedling stock in nurseries. *Forestry Chronicle* Vol. 36: 10-13.
3. Duryea, M. L. 1985. Evaluating seedling quality: importance to reforestation. In: Duryea M. L., editor. Evaluating seedling quality: principles, procedures, and predictive abilities of major tests. Corvallis (OR): Forest Research Laboratory, Oregon State University, p. 1-6.
4. Ivetić, V. 2013. Practicum for seed and nursery production and afforestation. University of Belgrade – Faculty of Forestry, 213 pp.
5. Jacobs, D. F., Woeste, K. E., Wilson, B. C., McKenna, J. R. 2006. Stock Quality of Black Walnut (Juglans nigra) Seedlings as Affected by Half-Sib Seed Source and Nursery Sowing Density.Proc. Vth Int. Walnut Symp. Eds. M.E. Malvolti and D. Avanza to *Acta Horticulturae* 705: 375-381.
6. Jacobs, F. D., Salifu, F. K., Seifert, R. J. 2005. Relative contribution of initial root and shoot morphology in predicting field performance of hardwood seedlings. *New Forests* Vol. 30: 235-251.
7. Krstić, M., Vojinović, N. 2002. Variability of some morphological characteristics of one-year-old seedlings of red oak, black walnut, birch and wild pear from the nurseries in the area of the mountain Jastrebac. *The Bulletin of the Faculty of Forestry*, Vol. 86: 147-160.
8. Mattsson, A. 1996. Predicting field performance using seedling quality assessment. *New Forests*. Vol. 13: 223-248.
9. Mayer, Ž. 2011. Establishing cultures of black walnut (*Juglans nigra* L.) by generative propagation, *Forestry journal* No. 7-8: 391-397.
10. Mexal, J. G., Landis, T. D. 1990. Target seedling concepts: height and diameter. In: Rose R, Campbell SJ, Landis TD, editors. Proceedings, target seedling symposium, combined meeting of the western forest nursery associations. Fort Collins (CO): USDA Forest Service, Rocky Mountain Forest and Range Experiment Station. General Technical Report RM-200, 1990: 17-35.
11. Oliet, J. A., Planelles, R., Artero, F., Valverde, R., Jacobs, D. F., Segura, M. L. 2009. Field performance of P. halepensis planted in Mediterranean arid conditions: relative influence of seedling morphology and mineral nutrition. *New Forests*, Vol. 37(3): 313-331.
12. Oršanić, M., Drvodelić, D., Kovačević, I. 2007. Nursery production of black walnut (*Juglans nigra* L.) seedlings. *Forestry journal* no. 5-6, Vol. CXXXI: 207-217.
13. Roller, K. J. 1977. Suggested minimum standards for containerised seedlings in Nova Scotia.Department of Fisheries and Environment Canada, Canadian Forestry Service, Information Report M-X-69: 1-18.
14. Stilinović, S. 1960. Some considerations on the application of some methods for evaluating the quality of planting material in our conditions. *Forestry*, Vol. 13(1-2): 49-55.
15. Woeste, K. E., Jacobs, D. F., McKenna, J. R. 2011. Half-sib seed source and nursery sowing density affect black walnut (*Juglans nigra*) growth after 5 years. *New Forests*. Vol. 41: 235-245.

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CITY BIOMASS-FIRED HEATING PLANT – ENVIRONMENTAL IMPACT ASSESSMENT

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ABSTRACT

The project of constructing a biomass heating plant that is fired by wood chips as an energy generating product that represents a renewable source, from the aspect of environmental protection and preservation of non-renewable sources, gives an absolute advantage over classical thermal power plants that are fired by fossil fuels. Usage of wooden biomass provides energy independence from the imported energy generating products (heating oil) and achieves economic benefits. This environmental impact assessment was aimed at observing all possible environmental impacts (positive and negative) that occur during the implementation of a project, both during construction and during exploitation. Basically, acceptability assessment ensues from a relation between benefits and damages that a planned project would produce.

Key words: assessment, heating plant, biomass, environment.

INTRODUCTION

Today, the application of biomass for the production of energy is encouraged, taking into account the principle of sustainable development. Wooden chips, created as a by-product or waste, are most frequently used, as well as the remains that cannot be put to any other usage. Such biomass is used as fuel in plants for the production of electrical and thermal energy, or processed into gaseous and liquid fuels for vehicles or home consumption. Principal advantage of biomass over fossil fuels is incomparably lower emission of hazardous gases and waste substances (Đonlagić, 2010).[1]

In line with the Spatial plan for the City of Banja Luka (2011-2030), it is clear that the construction of thermal energy plants that use the so-called renewable energy sources (RES) is stimulated, it is to say biomass usage is promoted. On the other hand, BiH has adopted an Action plan for usage of renewable energy, which envisages a target share of energy from RES to amount up to 41% until 2020. [2] According to the proposal of this plan, until the end of 2018 residential sector needs to implement energy efficiency programmes/measures in order to achieve savings in the consumption of final energy of 5.25 PJ (125.4 ktoe) per year. If this trend continues until the year 2020 total savings should amount 6.41 PJ (153.1 ktoe). Exploitation of energy from some renewable sources is defined based on availability and usability of these sources is specific to every country, it is to say local community (Ahmad et all, 2016, Saidur, et al., 2011) [3,4]. In BiH, biomass is widely and almost equally distributed, with excellent technical potential. However, it must be used in a way that shall, in terms of energy, be more efficient and sustainable than so far, as it became a rule throughout the world long ago.

Existing condition of the heating system in Banja Luka is organised in a way that is works through a central heating oil-fired boiler room, with four boilers with a total capacity of 232 MW of installed power and two regional wooden chips-fired boiler rooms, notably: "Starčevica" with a total capacity of 10 MW of installed power (6+4 MW) and "Kosmos" with a capacity 6 MW of installed power. Existing heating oil-fired boiler room shall be kept as a reserve after the project completion, in technically operative condition as alternative.

Given a high price and unsustainable usage of energy, needs to convert to and use the RES and efficiently usage of energy have become priority. In BiH, biomass is widely and almost equally distributed, with excellent technical potential. Almost 53% of soil in BiH is covered with woods (about 2.7 million hectares); it is an assessment that about 1.785.000 m^3 of wooden waste is annually generated [5]. All projects that are considered to have possible negative environmental impacts require the elaboration of environmental impact assessments, including all environmental segments, both during the execution of works and during the exploitation period.

MATERIAL AND METHODS

Basically, acceptability assessment of planned plants ensues from a relation between benefits and damages that a planned plant would produce. For that reason all possible environmental impacts of the proposed project were analysed, both during the plant's construction and during its exploitation. In line with the required assessment of project's feasibility, possible project's impacts were determined according to the following criteria:

- according to the deadline of possible impacts during the plant's construction and during its exploitation,
- according to their duration, possible impacts are short-lasting, occasional, continual and irreversible,
- according to their distribution area, possible impacts are local, regional and global,
- impacts can be direct (area of the plant and works) and indirect,
- according to their significance, impacts are low, moderate, extensive and impermissible,
- according to favourability: hazardous/unfavourable and useful/favourable impacts.

Environmental impact assessment was developed in line with the Environmental Protection Law and Rulebook of factories and plants that can be constructed and commissioned only if they have the environmental permit. [6,7]

RESULTS AND DISCUSSION

Environmental impact assessment is a systematic identification and assessment of potential impacts of proposed projects on physical-chemical, biological, cultural and socio-economic components of the entire environment. The aim of the environmental protection during the execution of construction and reconstruction of diverse facilities is to identify, it is to say propose conditions that make environmental impacts to be within the law-prescribed permitted limits, as well as present practice at the level of profession and the level of socio-economic development.

Subject facility shall produce thermal energy from renewable sources, which provide a series of advantages over the environmental requirements, but also significant economic advantages, which conclusion can be drawn by comparing prices of the presently used energy generating product (heating oil) and the planned energy generating product (biomass, wooden chips). Existing condition of the heating system in Banja Luka is organised in a way that is works through a central heating oil-fired boiler room and two regional wooden chips-fired boiler rooms ("Starčevica" and "Kosmos"), hence the implementation of this project would make a complete transfer to biomass as neutral fuel.

Figure 1. Plots on which the construction of a biomass-fired heating plant is planned

The commencement of civil works, construction itself and exploitation of the plant shall have no impacts on protected cultural and natural values. Area of direct impacts is the area around the very facility. Area of indirect impacts is the area where no works shall be executed but where the environmental impacts of the plant are defined based on given criteria and measures. Possible indirect impacts are the impacts that would be achieved without additional technical and other protection measures.

Impacts expected during construction

Possible impacts expected in the period of construction are temporary land occupation, emission of gases from construction machines and transport means into the air and noise and vibration emission. The listed negative impacts during the execution of works are temporary and no significant disturbance of the environmental quality at the location is expected if the works are executed in line with good construction practice.

Since many noise-producing construction machines and transport means will be used during the construction a noise level may occasionally exceed the usual level of allowed noise at the border of residential zone 45 dBA. This especially refers to the period during the night in case of building and transporting in night hours. Noise that can be generated during the operation of machines impacts the fauna because it disrupts permanent stay of animals and makes them move away from noise sources (Barber, et al., 2011; Francis, et al., 2009). [8,9]

Direct and indirect impacts on surface waters and groundwater during the construction of a biomass-fired heating plant at subject location are possible due to inadequate solution to drainage and disposal of sanitary (faecal) waters, potential risk of spilling or incidental spilling of fuel and similar waste, uncontrolled deposition of excavated material, inadequate disposal of unused substances and their packaging. However, the mentioned negative impacts during the execution of works are temporary in character and no significant disturbance of the Vrbas river water or of groundwater is expected should the works be executed in line with good construction practice.

Air quality may be violated during the construction of a biomass-fired heating plant due to an increased concentration of dust particles in the air, which may have a negative impact on the surrounding vegetation. Values of the concentration of floating dust will mostly depend on preliminary preparation of terrain, moisture of surfaces and windiness. Such isolated dust is larger and settles over a short period at short distances from its emission source. The mentioned emissions have no continual character, and discharge of polluting substances into the air has a local and short-lasting character. These mentioned impacts have local character and generally can be reduced by a good organisation of works at the construction site.

A surface vegetation cover shall be removed during the preparation of location for the commencement of the project, which will also lead to the removal of autochthonous plants. Other areas shall be recultivated with autochthonous plant species in line with the landscaping project after the preparation of terrain and removal of plant species. Observing the project as a whole, impacts on plants and animals will only last during the plant construction, and will have a low intensity. Bearing in mind that no protected plant species are found in subject area, and that this is a relatively small area from the vegetation-habitat aspect, no plant species is expected to disappear in subject area.

Expected impacts during exploitation

Environmental impacts during exploitation are reduced by the installation of quality equipment, primarily bag filters with high efficiency, by installing adequate insulation materials, planning a round, passable direction of movement around the facility, by application of fire protection measures and measures of protection from the pollution of groundwater and surface water courses and automated operation of the plant. Environmental impacts caused by incidental situations can be expected in the occurrence of fire since this is a building where wooden chips is incinerated, with areas and silos for wooden chips storing.

Biomass-fired plant's commissioning shall have a positive impact on populace in the City of Banja Luka, which will reflect in the reliance of thermal energy supply that is simultaneously the most acceptable solution from the environmental aspect.

In addition to these effects, many indirect effects are expected, such as wider social impacts, it is to say hiring local providers of wooden chips; this will lead to an increase in employment, an increase in local consumption by direct inflow in the city's territory, as well as many environmental impacts since this project can be put on a list of projects that bring about decreases of the emission of hazardous gases into the atmosphere.

During its exploitation, it is to say active operation of city's wooden chips-fired heating plant, waste flue gases emission is expected from the boilers where biomass is incinerated. However, since the installation of a wooden chips-fired boiler dedusting system is planned this dedusting system is considered to represent optimal solution with the highest efficiency, and it is deemed that no air quality impacts shall occur. Impact of the planned city's biomass-fired heating plant on surface waters and groundwater during exploitation is insignificant given the plant type.

No direct impacts on soil area expected during the normal operation of subject plant, green areas shall be developed by planting autochthonous plant species after the city's heating plant is completed; where natural landscaping characteristics of surrounding area must be retained as much as possible, and existing vegetation must be preserved as much as possible, which will ensure the preservation of habitats. Construction of the biomass-fired heating plant is planned in a way that it is adapted to urban character of the plot, and in architectural and ambient terms is planned to fit into the city's urban image, thus it is considered to have no significant impacts on landscape areas. Results of the implemented assessment show:

- The most significant negative impacts are impacts that are expected during the period of construction, such as temporary land occupation, emission of gases from construction machines and transport means into the air, and noise and vibrations emission. Listed negative impacts during the execution of works have a temporary character and no significant disturbance of the environmental quality at subject location is expected.
- The construction of a biomass-fired heating plant will have the following benefits: an advantage of biomass is that it is a renewable energy source, meaning it cannot be consumed as is a case with fossil fuels, biomass helps reduce a total emission of greenhouses gases into the atmosphere, the

environment is cleaner because a large portion of waste is used to produce energy from biomass, and it is a fact that biomass is a widely accessible energy source.

CONCLUSION

After the implemented analysis of environmental impacts of the project for the construction of a biomass-fired heating plant, a conclusion can be drawn that, given the character of impacts and their significance, a certain level of environmental impacts of the planned plant exists. However, all these impacts can be reduced to acceptable limits by applying specific measures; thus it can be stated that the implementation of subject project can provide conditions necessary for environmental protection.

REFERENCES

1. Đonlagić, M., Study of renewable energy sources in BiH, Centre for ecology and energy, Tuzla, 2010.
2. National renewable energy action plan BiH (NREAP BiH)
3. R. Saidur, E.A. Abdelaziz, A. Demirbas, M.S. Hossain, S. Mekhilef: *Renewable and Sustainable Energy Reviews*, Volume 15, Issue 5, Pages 2262-2289. 2011. (https://doi.org/10.1016/j.rser.2011.02.015)
4. A. A. Ahmad, N. A. Zawawi, F. H. Kasim, A. Inayat, A. Khasri: Assessing the gasification performance of biomass: A review on biomass gasification process conditions, optimization and economic evaluation, *Renewable and Sustainable Energy Reviews*, Volume 53, Issue null, Pages 1333-1347, 2016. (https://doi.org/10.1016/j.rser.2015.09.030)
5. V. Doleček, I. Karabegović: Biomass as energy potential of renewable energy sources in BiH, International online conference on forest agricultural fires as one of significant causes of climate changes, 2013.
6. Environmental Protection Law (RS Official Gazette, No. 71/12, 79/15).
7. Rulebook of factories and plants that can be constructed and commissioned only if they have the environmental permit (RS Official Gazette, No. 124/12).
8. Barber, J.R., C.L. Burdett, S.E. Reed, K.R. Crooks, D.M. Theobald, K.M. Fristrup: Anthropogenic noise exposure in protected natural areas: estimating the scale of ecological consequences. Landscape Ecology 26, 1281-1295. 2011.
9. Francis, C.D., C.P. Ortega, A. Cruz: Noise pollution changes avian communities and species interactions. Current Biology 19, 1415-1419. 2009.

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THE NORTH ATLANTIC OSCILLATION (NAO), THE ARCTIC OSCILLATION (AO) AND FOREST FIRES IN LITHUANIA

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ABSTRACT

In Lithuania in the period 1992–2015, decreasing trends were recorded for the annual number of forest fires (significant at $p \leq 0.05$) and the annual burned area (not significant). In the research of the connection between forest fires and the North Atlantic Oscillation (NAO) index, the highest values of Pearson correlation coefficient (significant at $p \leq 0.01$) were recorded for the annual number of fires and NAO index for June (0.589) and summer (0.538). With the Arctic Oscillation (AO) index, the highest value was recorded for the annual number of fires and AO index for June (0.486).

Key words: forest fires, Lithuania, NAO, AO.

INTRODUCTION

Forests cover 2,173,000 ha (33.3%) of the territory of Lithuania. Conifer stands constitute 56.1% of forest area. The most widespread species is Scots pine (38% of forest area), followed by spruce (24%) [1]. Despite significant presence of coniferous species very endangered by fires, Lithuania could be considered less affected by fires. Smaller fires are typical for this country and in 2015 only 8 fires bigger than 1 ha were recorded [2]. Factors which determine fire frequency and size could be climate influences of the North Atlantic Oscillation (NAO) and the Arctic Oscillation (AO).

NAO index is calculated on the basis of the difference in sea surface air pressure between Iceland (low) and the Azores (high). It is characterized by both a positive and a negative phase. Strong positive phase is connected with above-normal temperatures across northern Europe. On the other side, it is also associated with above-normal precipitation over northern Europe and Scandinavia. Opposite patterns of temperature and precipitation anomalies are typically observed during strong negative phases of the NAO [3].

AO index is calculated on the basis of the difference in air pressure between 45° N (high) and above Arctic (low). It is also characterized by both a positive and a negative phase. When the AO is in the positive phase, strong winds circulate around the North Pole. This belt of winds becomes weaker and more distorted in the negative phase of the AO, which allows an easier southward penetration of colder, arctic air masses that cause increased storminess in the mid-latitudes [4].

The main aim of this research is the analysis of the connection between these teleconnections and forest fires in Lithuania. The analysis of forest fire trends on the basis of available data was also conducted.

DATA AND METHODS

The main source of the data on forest fires was the European Commission report [2]. The data on forest fires in Lithuania (period 1992–2015) cover:

- the annual number of forest fires – N;
- the annual burned area – P;
- the average burned area per fire – A.

For these datasets linear trends were determined. In addition, statistical significance of linear trend was determined for (n-2) and on the basis of the coefficient of determination (R^2). For the testing of the significance t test was used:

$$t = R\sqrt{\frac{n-2}{1-R^2}}$$

where n – the length of the series.

Monthly and seasonal values of NAO index and AO index were used in the research. The data were downloaded from the Earth System Research Laboratory, National Oceanic & Atmospheric Administration, U.S. Department of Commerce [5, 6].

For the calculation of correlation Pearson correlation coefficient (R) on the basis of linear trend was used. Statistical significance was tested on $p \leq 0.05$ and $p \leq 0.01$. Calculation did not use the data for the period October to December, since fire season in Lithuania is in the period April–September [2].

RESULTS AND DISCUSSION

In Lithuania in the period 1992–2015, a decreasing trend of the annual number of forest fires was recorded (Figure 1). It was determined that the trend is statistically significant at $p \leq 0.05$.

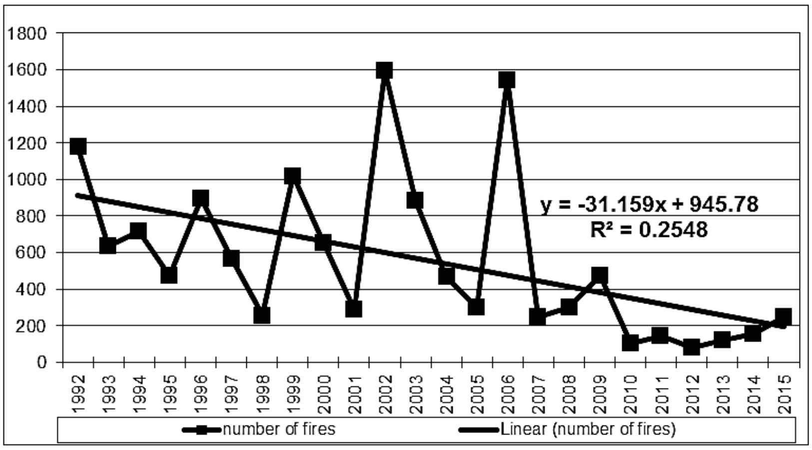

Figure 1. The annual number of forest fires in Lithuania (1992–2015) [2] with the trend line

A decreasing trend of the annual burned area was also noted (Figure 2). The trend is not statistically significant at $p \leq 0.05$.

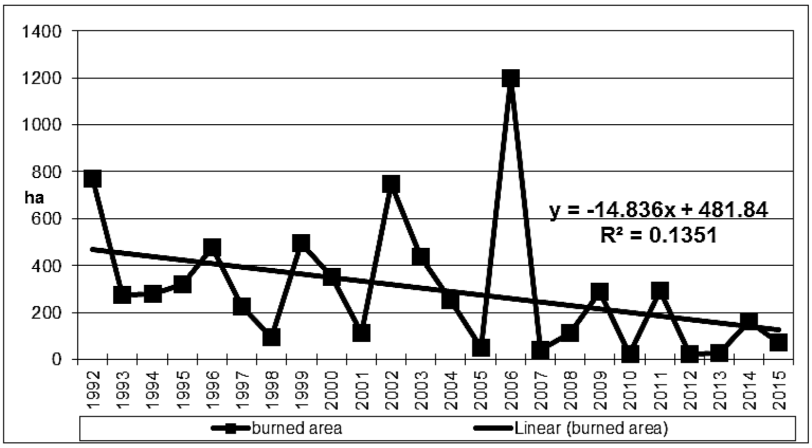

Figure 2. The annual burned area in Lithuania (1992–2015) [2] with the trend line

An increasing trend of the average burned area per fire was recorded (Figure 3). The trend is not statistically significant at $p \leq 0.05$.

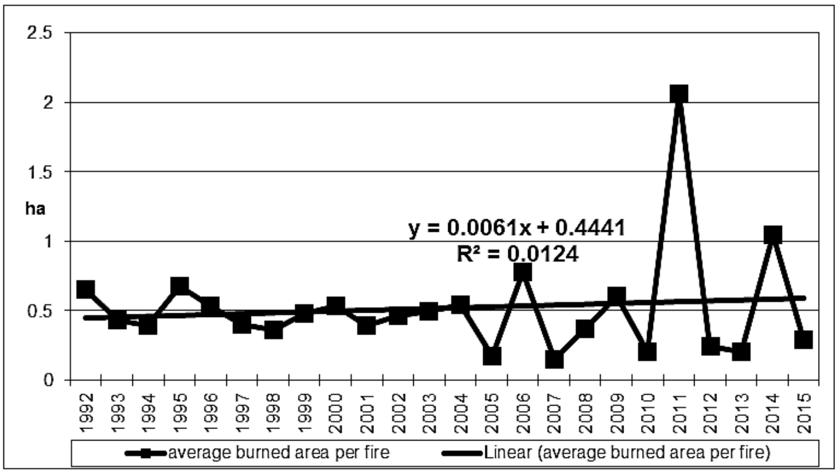

Figure 3. The average burned area per fire in Lithuania (1992–2015) [2] with the trend line

Lithuania is not much endangered by forest fires. In the period 1992–2015, the annual number of forest fires varied between 81 in 2012 and 1596 in 2002. The annual burned area varied between 20 ha in 2012 and 1199 ha in 2006. The average burned area per fire was below 1 ha in all years of the period, except in 2011 (2.06 ha) and 2014 (1.05 ha).

The results of the research of the correlation between forest fires in Lithuania and NAO index are shown in Table 1.

Table 1. Pearson correlation coefficient (R): Forest fires in Lithuania (1992–2015) – NAO index

	NAO index											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Winter	Spring	Summer
N	0.121	0.165	-0.023	0.232	0.221	0.589**	0.358	0.250	-0.343	0.024	0.208	0.538**
P	0.043	0.124	-0.075	0.365	0.204	0.515**	0.341	0.026	-0.308	-0.042	0.237	0.400
A	-0.351	0.269	0.132	0.506*	0.072	-0.041	-0.039	-0.368	0.218	-0.173	0.344	-0.196

* significant at $p \leq 0.05$;** significant at $p \leq 0.01$; N – annual number of fires; P – annual burned area; A – average burned area per fire.

The highest value of R was recorded for the annual number of fires and NAO index for June (0.589) (Figure 4). On the seasonal level, the highest value is for summer (0.538). These two values are significant at $p \leq 0.01$.

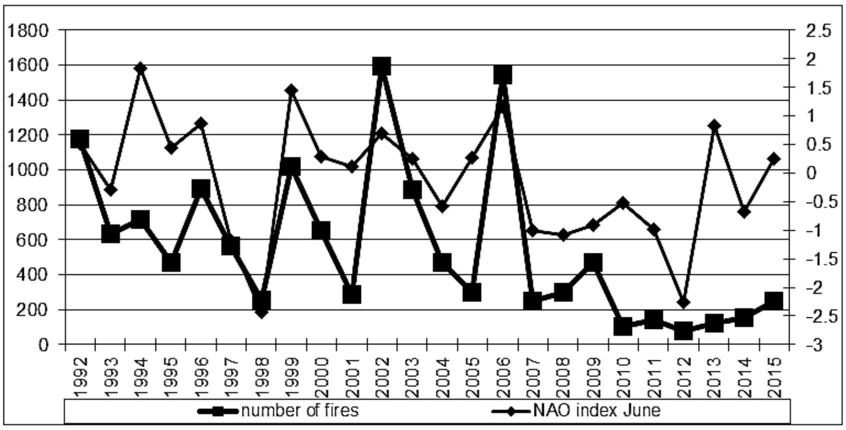

Figure 4. The annual number of fires in Lithuania (1992–2015) – NAO index for June: R=0.589 (significant at p≤0.01)

For the annual burned area the highest value of R was recorded in June (0.515) (Figure 5). The value is also significant at p≤0.01.

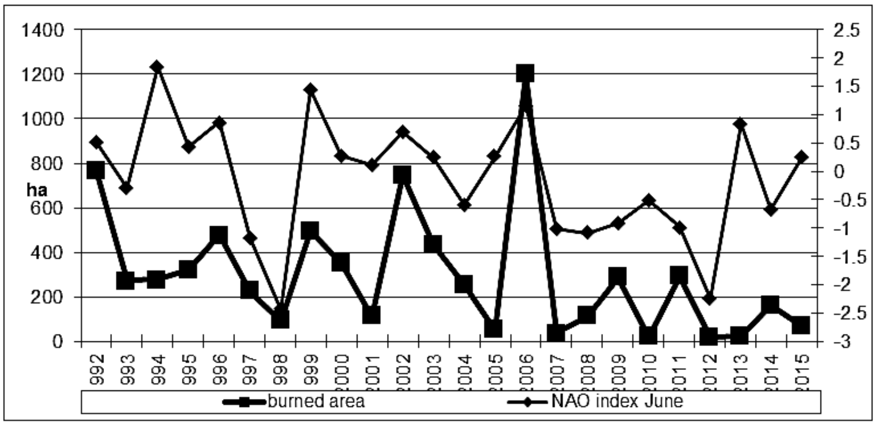

Figure 5. The annual burned area in Lithuania (1992–2015) – NAO index for June: R=0.515 (significant at p≤0.01)

For the average burned area per fire the highest R value was recorded in April (0.506). It is significant at p≤0.05.

The results of the research of the correlation between forest fires in Lithuania and AO index are shown in Table 2.

Table 2. Pearson correlation coefficient (R): Forest fires in Lithuania (1992–2015) – AO index

	AO index											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Winter	Spring	Summer
N	0.274	0.328	-0.066	-0.230	0.173	0.486*	0.359	0.017	0.021	0.183	-0.065	0.425*
P	0.135	0.343	-0.090	-0.135	0.205	0.400	0.285	-0.070	0.095	0.100	-0.030	0.313
A	-0.250	0.404*	0.236	0.468*	0.069	-0.198	-0.169	-0.433*	0.245	-0.056	0.369	-0.347

* significant at $p \leq 0.05$;** significant at $p \leq 0.01$; N – annual number of fires; P – annual burned area; A – average burned area per fire.

The highest value of R was recorded for the annual number of fires and AO index for June (0.486). For the average burned area per fire the highest R value was recorded in April (0.468). These two values are significant at $p \leq 0.05$.

In similar research, the Atlantic Multidecadal Oscillation (AMO) was brought into connection with forest fires in France [7] and Portugal [8]. Outside Europe, AO was brought into connection with the annual burned area and the average burned area per fire in Manitoba (Canada) [9]. The NAO positive phase is linked with increased wildfire activity in the central Gulf Coast (United States) [10]. El Niño-Southern Oscillation (ENSO), NAO, Pacific Decadal Oscillation (PDO), and Pacific-North American (PNA) showed significant correlations with wildfire data in the state of Mississippi. The combination of these teleconnection indices might form the basis for the creation of predictive fire-risk models [11].

Results of the research of the connection between the NAO index and the AO index on one side and forest fires in Lithuania on the other side could be the basis for future fire danger forecast. Similar research could be done in other European countries, but the research using other teleconnection indices is necessary. The use of forest fires datasets for longer periods (for example 40–50 years) presents a precondition for satisfactory results of the research.

Also, it should be kept in mind that a new theory on the causes of forest fires exists. According to this theory, forest fires are caused by highly energetic particles of solar wind, which penetrate through geomagnetic field and reach the vegetation on the Earth's surface [12–15].

CONCLUSION

In Lithuania in the period 1992–2015, the decrease of the annual number of forest fires was statistically significant at $p \leq 0.05$, while the decrease of the annual burned area was not. The increase of the average burned area per fire was not statistically significant at $p \leq 0.05$. Lithuania is not much endangered by forest fires. The average burned area per fire was below 1 ha in all years, except in 2011 and 2014. The highest values of Pearson correlation coefficient (significant at $p \leq 0.01$) were recorded for the annual number of fires and NAO index for June (0.589) and summer (0.538). Statistically significant values were also recorded for the annual burned area and NAO index for June and the average burned area per fire and NAO index for April. In the research with AO index, the highest value of R was recorded for the annual number of fires and AO index for June (0.486). Results of the research could be used in future fire danger forecast.

Acknowledgements

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REFERENCES

1. http://www.gmu.lt/forest_resources/
2. 2] San-Miguel-Ayanz, J., Durrant, T., Boca, R., Libertà, G., Boccacci, F., Di Leo, M., López Pérez, J., & Schulte, E. (2016). Forest Fires in Europe, Middle East and North Africa 2015; EUR 28158 EN; http://dx.doi.org/10.2788/914; http://forest.jrc.ec.europa.eu/effis/reports/annual-fire-reports/
3. https://www.ncdc.noaa.gov/teleconnections/nao/
4. https://www.ncdc.noaa.gov/teleconnections/ao/
5. https://www.esrl.noaa.gov/psd/data/correlation/nao.data
6. https://www.esrl.noaa.gov/psd/data/correlation/ao.data
7. Milenković, M., Ducić, V., Burić, D., Lazić, B. (2016). The Atlantic Multidecadal Oscillation (AMO) and the forest fires in France in the period 1980–2014. *Journal of the Geographical Institute "Jovan Cvijić" SASA, 66*(1), 35–44. doi: 10.2298/IJGI1601035M
8. Milenković, M., Yamashkin, A. A., Ducić, V., Babić, V., Govedar, Z. (2017). Forest fires in Portugal – the connection with the Atlantic Multidecadal Oscillation (AMO). *Journal of the Geographical Institute "Jovan Cvijić", 67*(1), 27–35. doi: 10.2298/IJGI1701027M
9. Milenkovic, M., Ducic, V., Babic, V., Krstic, M., Lazic, B. (2016). The connection between Arctic Oscillation (AO) and the forest fires in Manitoba province (Canada). In R. V. Pantovic & Z. S. Markovic (Eds.), *Proceedings / XXIV International Conference "Ecological Truth", Eco-Ist '16* (pp. 740–746). Bor: University of Belgrade, Technical Faculty.
10. Labosier, C. F., Frauenfeld, O. W., Quiring, S. M., Lafon, C. W. (2015). Weather type classification of wildfire ignitions in the central Gulf Coast, United States. *International Journal of Climatology, 35*(9), 2620–2634. doi: 10.1002/joc.4160
11. Dixon, P. G., Goodrich, G. B., Cooke, W. H. (2008). Using teleconnections to predict wildfires in Mississippi. *Monthly Weather Review, 136*(7), 2804–2811. doi: 10.1175/2007MWR2297.1

12. Gomes, J. F. P., Radovanovic, M. (2008). Solar activity as a possible cause of large forest fires —a case study: Analysis of the Portuguese forest fires. *Science of the Total Environment, 394*(1), 197–205. doi: 10.1016/j.scitotenv.2008.01.040, ISSN 0048–9697
13. Radovanović, M. (2010). Forest fires in Europe from July 22–25, 2009. *Archives of Biological Sciences, 62*(2), 419–424. doi: 10.2298/ABS1002419R
14. Radovanović, M., Vyklyuk, Y., Jovanović, A., Vuković, D., Milenković, M., Stevančević, M., Matsiuk, N. (2013). Examination of the correlations between forest fires and solar activity using Hurst index. *Journal of the Geographical Institute "Jovan Cvijić"SASA, 63*(3), 23–32. doi: 10.2298/IJGI1601035M
15. Radovanović, M. M., Vyklyuk, Y., Milenković, M., Vuković, D. B., Matsiuk, N. (2015). Application of adaptive neuro-fuzzy interference system models for prediction of forest fires in the USA on the basis of solar activity. *Thermal Science, 19*(5), 1649–1661. doi: 10.2298/TSCI150210093R

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TRACE THE MAN TO THE RIVER CONTROL WATER QUALITY OF MINERAL RESOURCES OF BRESTOVAC SPA

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ABSTRACT

This paper presents an overview of the state of Brestovac river and mineral springs water. Is done monitoring the quality of the mineral sources using natural, non-specific and microbiological indicators of water quality. Included are two points on Brestovac river, in the spa after the Pujica river flows and before mentioned river flows below the first settler. Based on the results, which were made in June 2015 and September 2016, obtained the status of water has deteriorated compared to the studies, which were conducted in the late nineties. They are now between II and III class quality.

Key words: thermo-mineral springs, Brestovac river, Brestovac spa, water quality.

INTRODUCTION

Within the project "Tracing the man to the river," conducted the hydroecological tests Brestovac rivers and thermal springs. The aim of this study was to determine the influence of man and waste water in the thermal mineral springs and Brestovac river. Based on the variety of physical and chemical characteristics of the mineral water in Serbia, it can be concluded that Serbia one of the richest region, which are at least a mineral water bottling exploited to [1]. Using thermal springs with one of the oldest forms of utilization of natural resources [2, 3]. On the territory of Eastern Serbia there are a number of mineral, thermal mineral, gas-rich, hot and cold springs and wells, whose water people traditionally considered medicinal, but modern medicine acknowledges in spa treatment in appropriate spa. The minerals contained in thermal waters are of volcanic origin.

HISTORY AND IMPORTANCE OF BRESTOVAC SPA

Brestovac thermal mineral water spa known since Roman times. It is assumed that the Romans around mined and used water. From the time of Turkish rule remained numerous traces of use of the spa, but prince Milos attached Brestovac spa as great importance. According to his wish in spa stayed Baron Herder in 1835, who first did the analysis of thermal waters. From this period, thanks to its characteristics, the spa is every day more and more developed and became known outside our borders. Spa water include: idrotin gas, sulfur-acid lime, sulfuric-acid iron, and somewhat bitter salts. The environment is pleasing to the eye, there are a lot of people, a lot of favorable conditions for life. Asserts that the water sources of similar composition. In Brestovac spa three most famous water: water eye, water for the stomach, and water for the nerves.

RESEARCH METHODOLOGY

Depending on the type of water, the samples are taken for testing from the sources, tap water, from a well, a lake or river [4]. Although it is assumed that the water samples homogeneous composition usually not the case. Water sample for testing shall be representative, which means that the composition of the sample should correspond to the composition of water in the examined cross section and a given time. Representative sample depends on the choice of sampling points, time, mode, sampling frequency, the water flow as well as ways of keeping the sample until ready for analysis [5] Have been used three ways of sampling and that are affected by (current) sample, which is determined by the volume of water entrained within a certain time, at a certain place, mixed (composite) pattern, which is a mixture of the single of the samples which were taken at certain time intervals or continuously in the course of a certain time from the test location and the total (aggregate) sample, which is assigned to the individual stirring of the samples which were taken at the same time from different places and depths.

Figure 1. Sampling of water on the ground

RESEARCH RESULTS

For practical, and the experimental section are used, the samples from the bone and to Brestovac water from three sources: water 1 – thermal water source for the nerves, water 2- thermal water source for eyes and water 3- thermal water source for the stomach. The survey was conducted in June 2015 and September 2016. After the water sample, we measured pH value and the temperature (Table 1), specific electric conductivity, turbidity, determination of the consumption of potassium permanganate, the chloride content, alkalinity and acidity and water total hardness. Table 2 shows the parameters, which have been tested for the aforementioned sources of water.

Table 1. Measured temperature value

	Temperature of water (°C)	Temperature of air (°C)	Measurement time (h)
Water 1	31	17	07:23
Water 2	33	18	07:38
Water 3	37	17	07:50

Figure 2. Measurement of the water temperature

Table 2. Parameters affecting water quality and are tested for the supplied water

Parameter	Water 1	Water 2	Water 3	Unit
Temperature of water	31	33	37	°C
Turbidity	0.06	0.06	0.12	/
Consumption of $KMnO_4$	2.5456	3.5002	2.5456	mg/dm^3
Electric conductivity	1021	1005	1009	µS/cm
pH	8.12	7.81	8.07	/
Alkalinity	12.9	21.8	60.4	mg $CaCO_3/dm^3$
Acidity	9.4	40.7	14.50	mg $CaCO_3/dm^3$
Total hardness	12.006	12.54	11.78	°N
Chloride content	25	20	29	mg/dm^3

From the attached results can be seen that the thermal springs of Brestovac Spa very rich in minerals, which means that water and medicines. In order to improve water quality must be regularly monitoring (monitoring) of water and the environment as well as various chemical analyzes. Based on the previously-made analysis of [6, 7, 8] and the data in Table 2 it can be noted that all three sources of water include moderately hard water, also can be said that the chloride content is satisfactory. Due to the higher temperatures and pH values should the water be used for drinking, as the pH value of the drinking water of 7 - 7.4.

CONCLUSION

Although Brestovac Spa represents a tourist destination, it should be taken to ensure the cleanliness of the spa and its surroundings. It can be said that the Brestovac Spa full of garbage, you throw away the tourists and also the locals (Figure 3). The water in a spa pool are also contaminated solid waste (Figure 4). Suggestions protection are as follows: to act in accordance with the rules on environmental protection, place a larger number of containers and garbage cans, sanctioned by illegal dumping, work on landscaping, mineral water and the whole spa and carry out purification of water that is not potable [9, 10, 11].

Figure 3. Garbage in Brestovac Spa

Figure 4. Polluted water in a spa pool

REFERENCES

1. T. Petrović, M. Zlokolica-Mandić, N. Veljković, D. Vidojević, Hydrogeological conditions for the forming and quality of mineral waters in Serbia, Journal of Geochemical Exploration 107 (2010) 373–381
2. M. Joksimović, M. A. Pavlović, Conditions and possibilities of direct utilisation of thermal-mineral waters in Raska region, Serbia, Renewable and Sustainable Energy Reviews 32 (2014) 107–113
3. B. Tripković, K. Penezić, On-site and off-site in western Serbia: A geoarchaeological perspective of Obrovac-type settlements, Quaternary International 30 (2017) 35–44
4. JKP „Vodovod“ Bor, Quality parameters of drinking-water determination methods, October 2010
5. J. Baras, R. Petrović, Pollution and water protection, Zavod za udžbenike, Belgrade 2009
6. S. Nikolić (1997): Chemical characteristics Brestovac River, The scientific conference on natural values and environmental protection, Proceedings "Our ecological truth", 123-6
7. S. T. Apostolov, B. S. Ristić, Purification of waste water from the contents of chromium compounds in order to protect environment, Ekologika and scientific conference, Belgrade, 21-22 April (2000)
8. S. Apostolov, S. Nikolić, Hydroecological tests Brestovac River, Proceedings of the "Ecological true "VIII scientific conference on natural values and environmental protection, Soko Banja, 04-07. June (2000) 346-351
9. S. Nikolić S. Apostolov, Hydroecological examination of the middle course of the Crni Timok, Proceedings "Ecological truth" VIII scientific conference on natural values and environmental protection, Soko Banja, 04-07. June (2000) 352-357
10. S. Apostolov, S. Nikolić, Hydroecological tests Brestovac river Annexes II, Proceedings "Ecological truth" IX scientific conference on natural values and environmental protection, Donji Milanovac, 03-06. June (2001) 255-258
11. S. Nikolić, S. Apostolov, Hydroecological examination of the middle course of the Crni Timok II Annexes Proceedings works "Ecological truth" IX scientific conference on natural values and environmental protection, Donji Milanovac, 03-06. June (2001) 251-255

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THE ENERGY EFFICIENCY OF THE WINDOW, AND ITS DEPENDENCY ON THE PHYSICAL MODEL OF CONSTRUCTION OF THE WINDOW

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ABSTRACT

Here is shown the interdependence of geometric and thermodynamic properties of several types of windows of different sizes, from different materials by applying the principles of geometric modeling. It explains the procedure for the use of data necessary for the further implementation of the calculation for which is used a software package Microsoft Office Excel, directly from the model window which is made in the software package Autodesk Inventor Professional. Coefficients of thermal transmittance for all types of windows are calculated. It also shows comparative overview of heat transfer coefficient when windows are filled with air and argon. The analysis and conclusions have been made about the correct choice of the window materials, size as well as the selection of the gas that will be used for filling, all in favour of increasing the energy efficiency of the structure.

Key words: energy efficiency, single glazed, casement, heat transfer coefficient, window.

INTRODUCTION

Average residential building loses through the windows about 36% of the energy needed to heat the building [1]. This means that the windows are, in terms of thermal isolation, weaker points in building covering, and therefore good places to improve the thermal performance of buildings and energy savings [2].

The window is made of glass, frame and, in some cases, of shading devices (blinds) and protection against insects (fly screen) [3].They play a crucial role in the construction of residential and commercial properties and should be constructed so as to achieve the greatest energy savings. Careful design can minimize energy losses.

Given that improving the thermal characteristics of windows is potentially large source of energy savings, it is necessary to make a calculation that would include as much data as possible on materials used for making the frame and the glass windows, of the gases that fill the chamber in window profiles, the standard windows dimension, etc. Such database could be used to choose the materials that will meet the required structural and energy requirements.

The aim is to make the calculation of heat transfer based on the geometric characteristics of the given frame, and therefore the glass windows, which provides insight into the best design of the window, frame material and the type of gas to be used in order to get the most energy efficient windows. That is to say, structure of the window with all the geometric characteristics should be modeled according to the required material selection, type of windows and a given coefficient of heat transfer, using the software package Autodesk Inventor Professional which pulls the required data from Microsoft Office Excel.

THE FORMULATION OF THE PROBLEM

The geometrical model for window costruction

To carry out simulation and analysis of the problem of heat propagation one must first construct a physical model of the window. For the modeling of mechanical elements and structures various tools can be used ie. various software for geometric modeling elements that are available on the market.

To show the window model in this paper software package Autodesk Inventor Proffesional was used which presents one of many of affordable tools for modeling the structure, technical documentation, as well as the the simulation of assemblying individual components, which form the window.

For the calculation of the heat transfer standard models of windows of different dimensions were observed and they are given in Table 1:

Table 1. Types of windows

GLASS	TYPE OF THE WINDOW	*WINDOWS CASEMENT*	
GLASS	FIXED SINGLE GLAZED	SINGLE CASEMENT	DOUBLE CASEMENT
	FIXED DOUBLE GLAZED		
LOW E GLASS	FIXED SINGLE GLAZED		
	FIXED DOUBLE GLAZED		

As possible materials for making a window frame wood, aluminum and plastics (PVC) were considered. We analyzed the single-glazed windows and a fixed double-glazed with fillings between the panes, which were filled with air or argon.

The dimensions of the window frame and glass were choosen on the basis of technical documentation provided in the catalog of the manufacturer for windows and doors, [4].

Window profile was designed with the software package for modeling of mechanical structures and assemblies Autodesk Inventor Professional. Figure 1 shows the three-chamber frame profile that was created in order to calculate the heat transfer coefficient. Window profiles frames which are made of wood are single-chambered and those made of aluminum and plastic (PVC) are three-chambered.

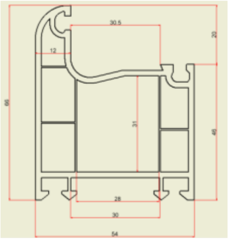
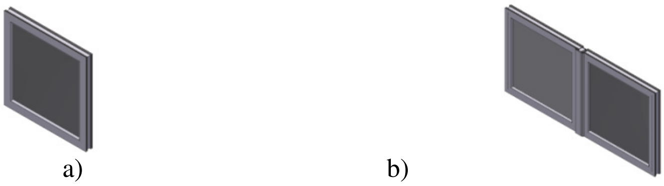


Figure 1. Three-chambered window profile frame

Models of ready-made windows are shown in Figure 2.



a) b)

Figure 2. Models of ready-made windows: a) single glazed window with single casement; b) single glazed window with double casement.

Active surfaces that will participate in the propagation of heat through the window were, after modelling, exported as data to software package Microsoft Office Excel using the package Autodesk Inventor Professional where the data will be used for further calculation of heat transfer.

Thermal analysis of thermal transmittance

The heat is spread through the window in three ways: through the conductive and convective ways due to the temperature difference of external and internal air and radiation from long-wave radiation (above 2500 nm) between the window and the environment, and between the glass layers, as well as of short-wave radiation (less than 2500 nm) that stimulates from the Sun, directly or reflected from the ground and adjacent structures.

Under the assumption that the temperature of the surface that radiate (sky, earth and surrounding objects)is equal to the temperature of the outside air, the basic equation of heat exchanged through the window is [2]:

$$q = U_w \cdot A_t \cdot (T_{out} - T_{in}) + E_t \cdot (A_g \cdot F_g - A_f \cdot F_f) \ , \qquad (1)$$

where: U_w- heat transfer coefficient of windows, T_{out} - external air temperature, T_{in} - internal air temperature, A_t - total surface of the window, A_g- glass surface (transparent), A_f - surface of the frame (opaque), F_g - the solar heat gain coefficient of the glass, F_f - the solar heat gain coefficient of the frame and E_t - total incident radiation.

Quantities U_w, F_g and F_f are considered to be constants, although they feature variable of the environment, where the most important are the temperature and wind speed. The temperature change due to weather conditions is small on an absolute temperature scale and it controls the size of the heat transfer by radiation. Solar heat gain coefficients depend on the angle at which sunlight falls.

If there is no sunlight, air infiltration and condensation, the first member of the equation (1) represents the size of the thermal heat transfer through the window system. Most systems consist of multiple transparent glass units and the opaque casement and frame, which together are called frame.

The coefficients of heat transfer for windows depend on: the material of the window frame [5] (wood, aluminum, plastic), frame construction (interruption of heat bridges or not), type of glazing [6] (single, double, triple glazing, low-e glass, the distance between glass, filling the space between ...).

Heat transfer coefficient of the window can be calculated if we know the coefficients of thermal conductivity of individual window elements, [2]:

$$U_w = \frac{A_{cg} \cdot U_{cg} + A_{eg} \cdot U_{eg} + A_f \cdot U_f}{A_{pf}}, \qquad (2)$$

where: U_{cg}, U_{eg}, U_f- coefficient of heat transfer for the glasscenter, edges of the glass and the frame, respectively, A_{cg}, A_{eg}, A_f- surface of the glasscenter, edges of the glass and the frame, respectively, and A_{pf}- surface of the aperture for the window minus the gap assembly.

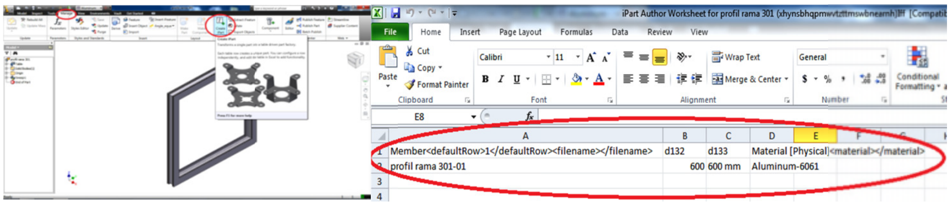
The values for the coefficients of heat transfer for the glass center glass, U_{cg}, depend on the structural characteristics of glazing, such as the number of glass panes, the dimensions of the space which is filled with gas, orientation with respect to the vertical, the radiation on each surface and the gas that fills the space between the glass plates. The thermal properties of transparent construction elements are given in Table 3 [7].

Heat transfer of the edges of the glass is two-dimensional and requires detailed modeling for the precise determination. Based on a detailed two-dimensional modeling [8] correlation has been developed to calculate the coefficients of thermal conductivity of the edge of the glass as a function type spacers and heat transfer coefficients of the center of the glass.

Window frames consist of casements, column, window boards, clips and spacers of the glass plates [9]. Determination of heat transfer through the frame is affected by: window type, material used for making frames, window size, width and type of glass spacers [2]. Regarding the type, windows can be windows with casements, sliding or fixed windows, doors leading to the garden, skylights, etc. The materials typically used for frame elements are wood, aluminum and vinyl [2].

RESULTS AND DISCUSSION

The data required for thermal analysis of heat transfer, the active surface of the window frame and the glass surface, can be read directly from the model. After constructing the model window, Figure 3 shows the couplement of software package that is used for modelling and another software package, by which the calculation of heat transfer was done.



	A	B	C	D	E
1	Member<defaultRow>1</defaultRow><filename></filename>	d132	d133	Material [Physical]<material></material>	
2	profil rama 301-01	600	600 mm	Aluminum-6061	
3					
4					

Figure 3. The couplement of software package Autodesk Inventor Proffesional and Microsoft Office Excel

Figure 3 shows that the necessary data, the active surface of the structure involved in the transfer of heat through the window, are labeled and further defined in the table with parameters within Autodesk Inventor. Then, the formed table with data is exported in Microsoft Office Excel where further processing of data obtaines coefficients of thermal conductivity.

Calculation of heat transfer $U_w$depending on the type of windows, glazing, frame material, the type of glass is shown in Table 2.

Table 2. Coefficient of heat transfer for single glazed windows $U_{w.}$

HEAT TRANSFER COEFFICIENT U_w [W/m^{2}K]					
TYPE OF THE WINDOW	WINDOW	FRAME MATERIAL			FILLING
	GLASS	WOOD	PVC	ALUMINUM	AIR
FIXED SINGLE GLAZED	1.168	5.852	1.663	1.664	1.168
					ARGON
	0.799	5.483	1.294	1.295	0.799

Diagrams in Figures 4 and 5 show that we find the highest heat flux in the case of single glazed double casement wooden windows and the lowest is in fixed single glazed single casement aluminum windows.

We can come to the conclusion that through the wood, as the material of choice for making the window frame, the greatest amount of heat is lost, that is, in this case the heat loss is the greatest. The diagram shows that, plastic (PVC) and aluminum as material for making window frame, provide the best thermal isolation, that is, the heat loss is minimal.

The fixed windows with single glazing in which the heat flux has very little value are especially interesting because they provide considerable saving of thermal energy and thus contribute to increasing the overall coefficient of efficiency of the whole building.

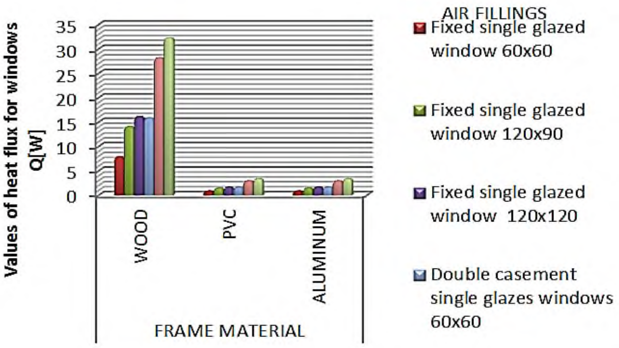


Figure 4. Values of heat flux for windows made of different materials, with different dimensions and air fillings

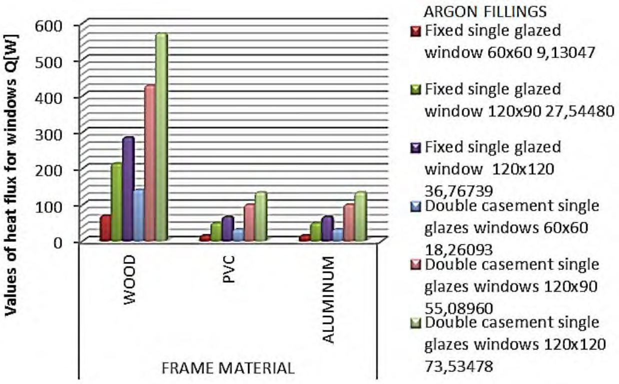


Figure 5. Values of heat flux for windows made of different materials, with different dimensions and argon fillings.

Diagram in Figure 6 and show the comparative heat transfer coefficient for single glazed window construction. It can be concluded that the fixed single glazed windows made of plastic (PVC), which are filled with argon fill, receive the lowest value for heat transfer (U_w=1,294 W/m^{2}K) but they achieve the best isolation ie. heat losses have the lowest value.

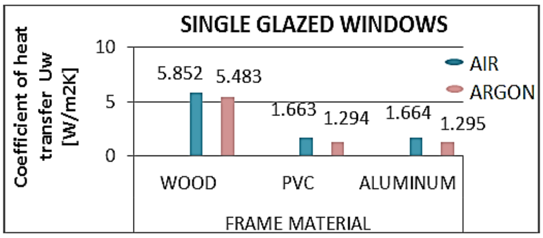


Figure 6. Values for coefficient of heat transfer for single glazed windows made of different materials, different dimensions and with different fillings

CONCLUSION

Windows play a crucial role in the construction of residential and commercial properties and should be constructed so as to achieve the greatest energy savings. Therefore, it is necessary to make a calculation that would include as much data as possible on materials used for making the frame and the glass windows, of the gases that fill the chamber window profiles, the standard dimensions of windows, on the basis of which to chose those materials that will meet structural and energy requirements.

Based on the given geometrical characteristics of the frame, and therefore of the glass of the window the calculation of heat transfer is done. Results that provide insight into the best design of the window frame material and the type of gas to be used in order to achieve the best heat transfer coefficient are derived from the calculation, ie. the largest value for U_w.

Based on the results presented in this paper we can conclude that the maximum value of heat transfer is obtained when using plastics to create a window profile which are filled with argon filling that has a much higher resistance to the propagation of heat from the air.

Responsible for the english language Sandra Vaskovic, ELT

REFERENCES

1. Pravilnik o energetskoj efikasnosti zgrada, Službeni glasnik RS, br. 61/2011
2. Gustavsen, A., Arasteh, D., Jelle, B. P., Curcija, C., Kohler, C., Developing low-conductance window frames: capabilities and limitations of current window heat transfer design tools - State-of-the-art review, Vol. 32 (2), pp.131-153, Journal of Building Physics, 2008
3. Škobalj, D., Prozori, Vol. 11, pp.24-32, Build, 2009
4. http://www.roloplast.rs/index.php/rs/katalozi/tehnicki katalog/book/1/Array?page=1 (visited 16.10.2016.)
5. Asdrubali, F., Baldinelli, G., Bianchi, F., Influence of cavities geometric and emissivity properties on the overall thermal performance of aluminum frames for windows, Vol. 60, pp. 298-309, Energy and Buildings, 2013
6. Van Den Bergh, S., Hart, R., Jelle, B. P., Gustavsen, A., Window spacers and edge seals in insulating glass units: a state-of-the-art review and future perspectives, Vol. 58, pp. 263-280, Energy and Buildings, 2013
7. Lyons, P., Arasteh D., Huizenga, C., Window Performance for Human Thermal Comfort, pp. 1-14., In Proceedings of 2000 ASHRAE Winter Meeting, Dallas, TX, February 5-9, 2000
8. Gustavsen, A., Griffith, B. T., Arasteh, D., Natural Convection Effects in Three-Dimensional Window Frames with Internal Cavities, Vol. 107 (2), pp. CI-01-5-1-11 ASHRAE Transactions, 2000
9. N. Cardinale, N., Rospi, G., Cardinale, T., Numerical and experimental thermal analysis for the improvement of various types of windows frames and rolling shutter boxes, Vol. 6(2), pp. 101-110, International Journal of Energy and Environmental Engineering, 2015

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MONITORING OF PHOTOCHEMICAL SMOG IN NIS IN THE FIFTEEN - YEAR PERIOD

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ABSTRACT

The aims of this paper were: to establish ozone concentrations in Nis in the fifteen year period, as well as concentrations of ozone precursors (nitrogen oxides and formaldehyde) in the same period, and to monitor their trend. In this investigation it has been found concentrations of ozone, nitrogen oxides and formaldehyde which were below of the guideline values. The mean values of ozone concentrations were between 1.11 $\mu g/m^3$ and 14.20$\mu g/m^3$, the mean values of nitrogen oxides concentrations were between 15.40$\mu g/m^3$ and 36.70$\mu g/m^3$, and formaldehyde concentrations were between 1.70$\mu g/m^3$ and 9.85$\mu g/m^3$. Ozone, formaldehyde and nitrogen oxides were showed increasing trend in the period examination.

Key words: ozone, formaldehyde, nitrogen oxides.

INTRODUCION

Photochemical smog forms in the lower atmosphere (troposphere) when sunlight hits high concetrations of nitrogen oxides and volatile organic compaunds, which promotes a series of photochemical reactions that lead to the formation of ozone.

Photochemical smog appears in clear, sunny days with low humidity of the air, in the presence of high concentrations of pollutant.

One of the most important pollutant, which is produced in the atmosphere by photochemical reactions, is ozone. Ozone has important detrimental health effects on humans. Because ozone is highly reactive, it has the ability to oxidize and destroy lung tissue. Acute O_3 exposures cause pulmonary function decrements, school absenteeism in children, injury and inflammation, cardiovascular events, and disease exacerbation, while chronic exposures to O_3 have been associated with increased incidence of asthma, diminished lifespan, and increased mortality due to cardiovascular and pulmonary disease, as well as reproductive effects (1).

AIM

The aims of this paper were:

- to establish ozone concentrations in Nis in the fifteen-year period (between 2002-2016)
- to establish concentrations of ozone precursors (nitrogen oxides and formaldehyde) in the same period,
- to monitor trend of ozone, nitrogen oxides and formaldehyde.

METHOD

Institute for Public Health Nis started monitoring of photochemical smog in 1992. on the one place in the town. Sampling of ambient air and laboratory testing was performed by acredited methods and test results were interpreted in according with the valid legislation

Results of examination are given in μg/m^3. In this paper are given some of the statistical parameters: mean values, percentiles (C50 i C98) in the period examination.

RESULTS AND DISCUSSION

In the period examination, the mean values of ozone concentrations (Table-1) were between 1.11 μg/m^3 (2014) and 14.20μg/m^3 (2016). The noticed values are below of the values which are given in the Regulation of Guidelines Values of Imission (85μg/m^3) in that period.

Table 1. Ozone concentrations in Nis between 2002-2016 (μg/m^3)

Year	X	Min	C_{50}	C_{98}	Max
2002	8.47	0.10	10.20	26.30	60.50
2003	10.03	0.40	7.50	20.90	30.70
2004	8.26	0.10	6.70	22.60	46.20
2005	9.07	0.10	7.60	26.60	36.70
2006	8.40	0.10	7.50	21.20	38.40
2007	3.07	0.40	2.20	12.38	41.00
2008	4.04	0.40	2.80	14.10	20.30
2009	8.54	0.80	7.70	21.50	36.70
2010	8.90	0.10	7.00	21.20	28.10
2011	7.80	0.30	4.60	31.60	56.80
2012	5.70	0.40	3.50	49.00	49.00
2013	8.80	0.20	8.10	20.90	52.60
2014	1.11	3.30	11.20	20.00	27.30
2015	14.00	5.60	11.70	47.40	47.40
2016	14.20	5.00	10.60	29.10	99.10

Nitrogen oxides concentratios are mainly below guideline values (Table -2). The mean values were between 15.40μg/m^3 (2011.) and 36.70μg/m^3 (2013.) while the percentile C_{98} values were between 20.40 μg/m^3 and 394.00μg/m^3.

Table 2. Concentrations of Nitrogen oxides in Nis between 2002-2016 (μg/m^3)

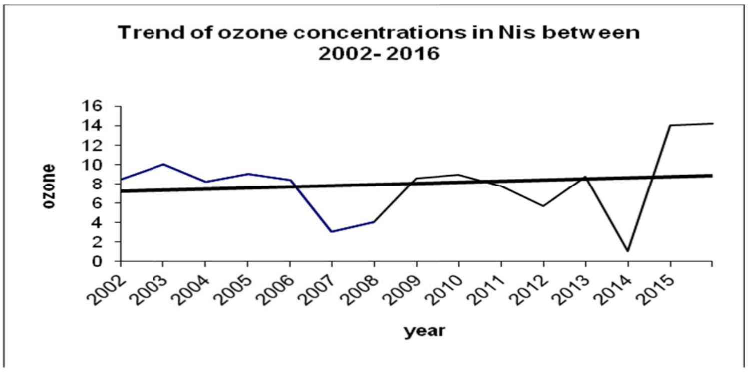
Year	X	Min	C_{50}	C_{98}	Max
2002	24.19	0.10	16.30	106.20	138.30
2003	20.85	6.50	19.80	42.70	58.80
2004	17.36	2.10	17.00	38.00	50.60
2005	22.57	0.80	20.40	20.40	40.80
2006	24.01	3.20	22.00	50.20	125.70
2007	17.98	0.50	17.50	90.8	102.80
2008	25.31	1.60	22.90	44.00	229.70
2009	23.42	1.10	22.40	76.00	77.80
2010	30.20	0.90	31.10	46.70	53.60
2011	15.40	0.30	52.10	52.10	52.10
2012	22.40	1.20	22.80	40.20	40.20
2013	36.70	0.90	16.50	394.00	394.00
2014	30.60	1.00	26.85	132.60	132.60
2015	26.10	3.00	23.90	87.70	87.70
2016	30.30	3.00	32.90	61.60	61.60

With regard to formaldehyde, we can say that situation is similar. Formaldehyde concentrations are also below guideline values. Registrated concentrations are given in the Table 3.

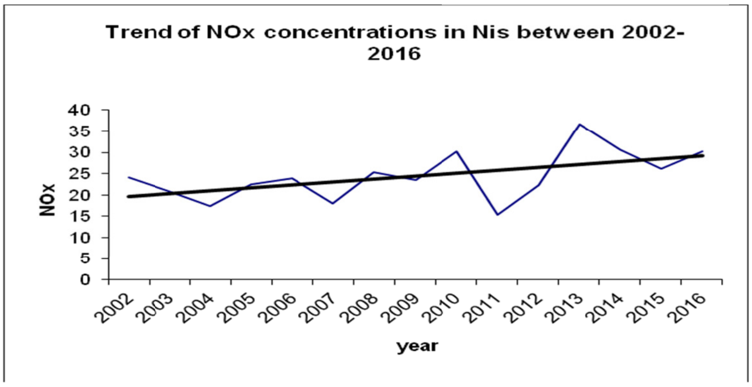
Table 3. Concentrations of formaldehyde in Nis between 2002-2016 (μg/m^3)

Year	X	Min	C_{50}	C_{98}	Max
2002	5.09	0.10	3.40	22.70	45.80
2003	4.04	3.03	3.00	17.90	32.40
2004	2.73	1.10	2.00	11.60	15.40
2005	4.71	0.10	3.20	20.10	25.30
2006	3.30	1.20	3.20	5.40	8.10
2007	1.93	0.90	1.50	4.40	4.90
2008	2.14	0.60	1.30	23.00	25.80
2009	9.85	2.00	9.70	19.30	26.80
2010	6.40	1.20	4.60	16.20	28.10
2011	2.50	0.3	1.50	1.20	12.50
2012	1.70	0.2	0.90	9.70	15.30
2013	4.6	0.1	1.20	59.20	109.00
2014	2.9	2.0	2.00	22	22
2015	<6.0	<6.0	<6.0	<6.0	<6.0
2016	<6.0	<6.0	<6.0	<6.0	10.20

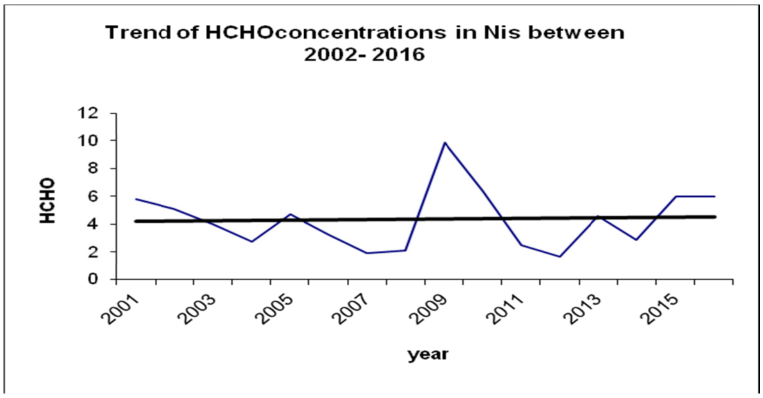
Trends of parameters are represented on the Graphics 1, 2 and 3. Ozone, formaldehyde and nitrogen oxides were showed increasing trend in the period examination.



Graphic 1. Trend of ozone concentrations in Nis between 2002- 2016



Graphic 2. Trend of NOx concentrations in Nis between 2002- 2016



Graphic 3. Trend of HCHO concentrations in Nis between 2002- 2016

CONCLUSION

In this investigation it hasn't been found concentrations of ozone, nitrogen oxides and formaldehyde which can have more important influence on the health of the people.

Mean values of concentrations of ozone and ozone precursors are below of the guidelines values.

In the fifteen years examination ozone, formaldehyde and nitrogen oxides were showed increasing trend. The probable reason for this is the increasing number of motor vehicles in Niš.

In consideration of toxicological importance of these parameters, we should continue their monitoring.

REFERENCES

1. National Institute of Environmental Health Sciences. Ozone induced Pulmonary Injury and Inflammation. Available at: www.niehs.nih.gov/research/atniehs/labs/lrb/envirogen/studies/pulmonary/index.cfm
2. Annual reports on air quality. Public Health Institute Nis

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ASBESTOS WASTE MANAGEMENT PROCEDURES AT THE TEHNICAL FACULTY IN BOR

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ABSTRACT

Asbestos was widely applied in industry, especially in the construction in the 70-ies of XX century due to its favorable physical and chemical properties, such as resistance to heat and fire, chemical inertness and mechanical properties. The inhaling of asbestos fibers very is harmful and causes malignant lung disease and asbestosis and because of that use of the asbestos has banned in the most of the countries in the world. The ban of asbestos use at the European Union (EU) started on January first 2005 (Directive 1999/77 / EC). In Serbia, the asbestos-containing material is present mainly in the form of so-called roof coverings asbestos panels and asbestos pipes in water supply networks. Alignment Serbian standards with EU standards produced the ban on the use of products containing asbestos fibers, prescribed procedures for managing waste containing asbestos and clear guidelines for removal, handling of asbestos waste and storage. The measures to prevent the dispersal of asbestos fibers were also prescribed. Licenses for managing of this type of waste have a few companies in Serbia, and because of that the costs for asbestos-containing material removing are high. The procedure for the asbestos-containing material removing from the one of the Technical faculty buildings is shown in this paper. The legal regulations that follow this procedure also were treated and preliminary costs are given.

Key words: asbestos, asbestos waste management, regulative of asbestos containing materials.

INTRODUCTION

The word "asbestos" (ἄσβεστος) is of Greek origin and means incombustible. Asbestos includes six hydrated silicate minerals belonging to the amphibole group: actinolite, amosite (brown asbestos), crocidolite (blue asbestos), tremolite and actinolite a group of serpentine chrysotile (white asbestos). The main characteristics of these minerals are that they have fiber structure, low thermal conductivity, resistance to flame and not burn. Asbestos – containing materials are the mostly used as insulators of heat, noise and vibration in construction and industry, but also are applied to households as insulation for water pipes, installed in the switch, as a car's brakes material, for firefighting suits, and so on.

There are significant deposits of asbestos in Serbia. Exploitation of asbestos has been carried out at two locations in “Stragari” mine, which was the largest asbestos mine in Europe, other asbestos mine “Korlaće” had a relatively modern plant for separation and ore processing. Both of mines have stopped further exploitation. Last available data for 2005 and 2006, when 4,080 tons in 2005 and 4,500 tons in 2006 of asbestos were produced [1]. The use of products containing asbestos was officially banned in 2011 in Serbia, but due to low prices and high mechanical resistance of asbestos products, it is still in usage in all parts of the country (30-70% of water supply networks made of asbestos pipes) and "asbestos" panel we can see on the roofs of buildings in all settlements. These products because of its wear resistance and durability are very present in the human environment and do not pose a risk while their structure is not disturbed. It is scientifically proven that the asbestos microfibers breathing results in three types of the disease: asbestosis, malignant mesothelioma and lung disease.

The main problem with asbestos fibers is that some of them are very small, with diameters of only ten nanometers. Owing to size, structural strength and chemical neutrality asbestos fibers easily penetrate the walls of cells and enter the nucleus itself to the "knotted" around the chromosomes. So, only mechanical, affect important of processes in which chromosomes are involved. The direct result of this interference in the chromosomes can produce malignant processes. The most sensitive are just the cells that build different lung tissue. The lung cancer is often an occupational disease of employees who work with asbestos. Particularly dangerous cancer tissue pleura (mesothelioma), having a nearly 100% mortality. It has been determinated a lot of non-cancerous diseases, mainly caused by the reaction of human immune system to the presence of asbestos fibers in the body. The most important is a disease characterized asbestosis and, depending on the exposure level, practically leads to a slow choking the patient. The common characteristic of all of these lung diseases caused by asbestos is that the first symptoms appear upon exposure to decades, [2].

Existing asbestos products have to be removed from the working and living area. Properly remove this products means to act in accordance with the prescribed procedure to remove, transport of materials containing asbestos and the storage without consequences for the health of people. There are a licensed companies dealing with these matters and are the only ones accredited to remove hazardous waste containing asbestos. In Serbia, the procedures are described in the Regulations and Guidelines but the general public who are directly exposed with these problems is not sufficiently trained to comply with these rules but usually eliminates this waste improperly stored and disposed thereby endangering themselves and the people they know.

This paper describes a procedure of removing the asbestos from the roof of the Mining building of Technical Faculty in Bor. The procedure, required technical documentation and preliminary costs were analyzed .

WASTE ASBESTOS MANAGEMENT LAWS AND REGULATIONS

The European Parliament in 1976 adopted a Directive which limits the production and use of asbestos. According to Directive 1999/77 / EC (1999), all member states are obliged to completely ban the use of certain hazardous materials which include asbestos and by 1 January 2005 and until 15 June 2006 that its legal acts comply with this directive, [3].

EU directives related to advertising, the use and sale of asbestos are:

83/477 / EEC (1983) - the protection of workers from asbestos exposure
83/478 / EEC (1983) - advertising and use of asbestos
78/319 / EEC, 87/217 / EEC, 91/689 / EEC - measures to protect the environment from pollution by asbestos as well as measures to control the disposal of asbestos
67/548 / EEC (1991) - Classification of all types of asbestos
91/382 / EEC (1991) - reduction of the maximum allowable amounts of asbestos
90/394 / EEC (1990), - introduction of the substitution pattern of asbestos
91/659 / EEC - ban on the use of all types of asbestos fibers
2003/18 / EC - the protection of workers from exposure to asbestos[4].

The Republic of Serbia has prescribed the following documents relating to asbestos:

- Regulations on bans and restrictions of production, marketing and use of chemicals (Sl. Glasnik RS, 90/2013). These Regulations forbid the manufacture, marketing and use of asbestos fibers and products which these fibers intentionally added. Stipulates that products containing these fibers, when put into markets or use, must have further notification that contains asbestos fibers;
- Regulations on preventive measures for safe and healthy work when exposed to asbestos (Sl. glasnik RS 106/2009, 006/2010, 15/2010). In Section 1 of this Regulation states that prescribing minimum requirements that the employer is obliged to fulfill in ensuring application of preventive measures in order to eliminate or reduce to a minimum the risk of injury or damage to health of employees which arise or may arise in exposure to asbestos. Requirements that are required to comply with legal entities licensed to perform testing of working environment in the process of preventive and periodic testing of working environment and given the limits for exposure to asbestos;
- Regulation of the treatment of waste containing asbestos (Fig. glasnik RS, no. 75/2010), which prescribes the manner of packaging, the criteria, conditions, and final storage of asbestos-containing waste and other measures to prevent the dispersal of asbestos fibers and dust in the environment .

In Serbia, the manner of carrying out intermittent operations in which workers are exposed to dust of low intensity, which is derived from asbestos or asbestos-containing waste, it is clear prescribed by guidance (Guidance for working places where the execution of tasks in which the exposure of employees to the dust originating from asbestos or materials containing asbestos occasionally, low intensity (Sl. glasnik RS, no. 42/2016)). This document provides clear guidance to the contractor to which way the work is carried out that security measures must be implemented and what kind of protective equipment workers must use. It is also prescribed procedures and sampling of asbestos in the air, and proper disposal of asbestos waste.

PROCEDURE FOR REMOVING ASBESTOS MATERIAL FROM THE ROOF ON THE BUILDING ON THE TECHNICAL FACULTY IN BOR

The building of the Mining department of Technical faculty in Bor is located in Vojske Jugoslavije street No. 15. The building was built in the late 60s and it's a three-story building made of solid brick covered with "asbestos" pannels as showen on figure 1. The total building area, according to cadaster RS Republic Geodetic Authority, is 503 m2, the measured length of the base of the building is 30.01 m and 12.20 m of width, which gives 366.122 m^2. The surface of the roof covered with panels is 860 m^2.

Firstly it is necessary to obtain approvals and permits for the works of reconstruction of the roof of by the municipal administration. It is also necessary for at least 48 hours prior to transport waste to announce's Ministry of Agriculture and Environmental Protection that the quantity of asbestos to be transported and where and the position of storage. After that it is necessary to conduct the procedure of filling the Document on movement of hazardous wastes and inform the competent inspector.

Figure 1. Satelite photo of the building of the Mining department of Technical faculty in Bor

The procedure of fixing the roof consist the following steps:

1. Examination of corrugated board by authorized laboratories, and determining whether the same is free of asbestos, in the case of not containing the procedure is identical to that carried out for the removal of non-hazardous construction and demolition waste. In the case of asbestos-cement plates containing a hazardous asbestos procedure is :
2. Determination of the exact amounts of asbestos waste to be removed,

3. It is necessary to develop the project documentation for reconstruction of the roof,
4. Engage an authorized house to perform work on removing asbestos boards,
5. Engage an authorized house for works of packaging, transportation and disposal of asbestos waste,
6. Engage the construction company to create a new roof of a building according to the technical documentation, [5].

If any material consists asbestos and how many, is determined by the laboratory. We can certainly confirm that the asbestos panels located on the roof of the building of the Faculty of mining are asbestos product, but regardless of this fact when removing the panel it is necessary to analyze the material by an accredited laboratory. Asbestos fibers have no own energy and can not move, they tend to spread by the wind. In the external atmosphere asbestos fibers pose little environmental hazard. The greatest danger is indoors.

In future work we wil treat as it is a hazardous asbestos waste. It is necessary to determine the level of risk faced by the employees and students. Since the asbestos panels are on the roof of the building and that they are not broken or in any visible way damaged, they do not pose a threat to workers and college students. Most likely due to the age of the roof covering, the same need to be replaced. It is believed that it is useful in time to settle down the procedure governing this type of waste.

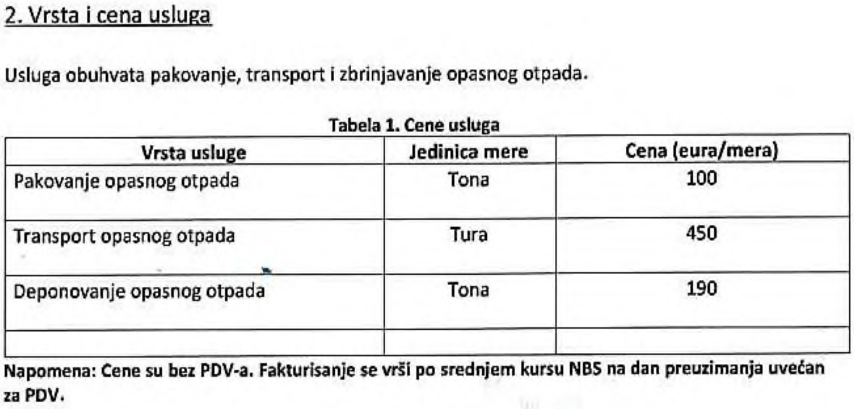
According to the procedure after determining the origin it is necessary to determine the amount of asbestos waste. It was found that on the roof of the building of the Mining Technical Faculty are 476 asbestos panels. The characteristics of these plates are shown in Table. 1 according to the manufacturer's catalog weight of one corrugated board is 15.60 kg which gives an amount of 7.50 tons of hazardous waste which has to be removed from the roof, packaged, transported and disposed of.

Table 1. The specification of the quantity of waste

Length [m]	1,25	Number of panel	7
Plate width[m]	1,05	Total number of panel	476
Useful length plate [m]	1,15	The length of the roof [m]	30,60
Usable width of panel [m]	0,90	Roof width[m]	14,70
Weight plates [kg]	15,6	roof surface[m^2]	480,42
Number plate lengthwise	34	The amount of waste [kg]	7.425,60

The process of disposal of asbestos waste involves high costs, primarily for the reason that the storage of this type of waste is only at two locations in Serbia, near Leskovac and in Vojvodina. Both are distant from the Bor, which further increases transport costs. Unlike some other types of hazardous waste from which they can obtain useful raw asbestos waste is not recycled but only permanently disposed of by an authorized company. Removing asbestos from the roof panel as hazardous waste, you can not do it alone but it is necessary to hire professionals with a license. This company will be under strict health and safety requirements to remove waste acting according to instructions.

For the disposal of asbestos waste at the site of Bor, according to preliminary offers companies engaged in this business, it is necessary to allocate EUR 100 / tonne for pakonje asbestos plate, 190 euros / tonne for the deposit and 450 euros / tour for the transport of asbestos plate as seen on Figure 2. Total costs per Specification amounted to 5 550,00 euros, which is only part of the amount that needs to be set aside for the rehabilitation of the roof.



2. Vrsta i cena usluga

Usluga obuhvata pakovanje, transport i zbrinjavanje opasnog otpada.

Tabela 1. Cene usluga

Vrsta usluge	Jedinica mere	Cena (eura/mera)
Pakovanje opasnog otpada	Tona	100
Transport opasnog otpada	Tura	450
Deponovanje opasnog otpada	Tona	190

Napomena: Cene su bez PDV-a. Fakturisanje se vrši po srednjem kursu NBS na dan preuzimanja uvećan za PDV.

Figure 2. Layout offers PWW DEPONIJA DVA DOO LESKOVAC authorized companies for packaging, transport and disposal of hazardous waste containing asbestos.

In addition to packaging, transport and disposal, it is necessary to hire a company that has a license and special equipment for removing plates from the roof, for which it is necessary to allocate additional funds.

In addition to the direct costs it is necessary to plan the costs for testing asbestos waste, preparation of technical documentation, obtaining permits municipal administration, etc

Building materials containing asbestos are still in use, mostly as an overlay roofs of residential buildings, schools, kindergartens and other facilities. Therefore, it is necessary to seriously undertake measures for its removal before damage occurs and release harmful asbestos particles. The state should propagate prevention and educate its citizens to independently recognize the danger.

Basic prevention guidelines include:

- The replacement of asbestos with other materials
- The ban on the continued use of asbestos!
- The list of facilities and installations that have asbestos.
- Strict procedures for asbestos removal
- Register of persons who have been exposed to asbestos, [6].

CONCLUSION

Damaged materials that contain asbestos are harmful to human health and should therefore be removed from man's environment. In our country are brought legal procedures that define this area, and are relevant to European standards. However, in practice, difficulties appear when applying the same. The problems are reflected in the lack of a large number of companies engaged in the removal, storage and disposal of such waste. Although there are more registered companies in this industry, most do not have the necessary conditions for the disposal of such waste. In this regard nessesary conduct stricter inspections of registered companies in this industry. Also, the state should be financially involved in the procedure of removing waste, especially from the educated and health institutions, generally from institutions that do not have their income and where they are exposed to hazards and young children. To successfully remove from the environment hazardous waste, which contains asbestos, it is necessary to involve individual legal entities which are in this business and also local government and the state.

REFERENCES

1. EURACTIV RS http://www.euractiv.rs/odrzivi-razvoj/3578-zabranjeni-azbest-i-dalje-opasnost (preuzeto 10. maja 2017)
2. B 92 http://blog.b92.rs/text/24413/Azbest/ (preuzeto 10. maja 2017)
3. Borislava Simendić, Vesna Petrović, AZBEST - PREVENTIVNE MERE ILI ZABRANA KORIŠĆENJA, Bezbednosni inženjering 2010 стр 39-42, Kopaonik 01-05 фебруар 2010.
4. Pravilnik o utvrđivanju profesionalnih bolesti, ("Sl. glasnik RS", br. 105/2003)
5. NE! AZBEST, http://neazbestu.org.rs/index.php/baza-znanja/category-blog/upravljanje-azbesnim-materijalima(preuzeto 12. maja 2017)
6. RARIS -REGIONALNA AGENCIJA ZA RAZVOJ ISTOČNE SRBIJE, http://www.raris.org/download/zivotnasredinazdravlje/Zdravstveni%20efekti%20izlo%C5%BEenosti%20azbestu_Prof.%20dr%20Petar%20Bulat.pdf(preuzeto 12. maja 2017)

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THERMOVISION APPLICATION IN TRIAGE PROCEDURES FOR EMERGENCY ORTHOPEDIC CONDITIONS

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ABSTRACT

In the paper is presented possibilities of thermovision application as a potential new diagnostic method in triage departments and services within health institutions of primary and secondary health care. Considerations are focused on orthopedic application with example of thermovision diagnosis on real patient with left knee joint problem. Main advantages of thermovision are highlighted as recommendations for including thermography as a very important diagnostic method. Also some disadvantages are pointed out as a reason why thermovision could be included in diagnostic procedures only as a kind of auxiliary method.

Key words: Diagnostic procedures, Thermovision, Thermal Imaging, Triage.

INTRODUCTION

Diagnostic centers are often dislocated from certain health departments or institutions. This means that orthopedic infirmaries and departments often must dislocate patients outside their jurisdiction in order to perform certain diagnostic actions with increasing the reaction time, which in some cases can be very critical. For example, in Serbia, many orthopedic cases are sent for examinations using magnetic resonance in diagnostic centers which are often more than a hundred kilometers away from the institution that is initiating the mentioned examination. Also there are a certain issues with scheduling and placement on the waiting list with a waiting period which in some cases is too long.

From the standpoint of patients who are referred to the aforementioned diagnostic examinations, there are concerns about transportation to the diagnostic center, but the most dominant issue is the economic one based on the financial component of every diagnostic exam. Diagnostic examinations can often be extremely financially demanding both for the patient as an individual and for various health insurance funds.

Patients and health institutions need new methods and new approaches in aim to avoid problems related to performing diagnostic exams nowadays. That new methods and approaches must reduce costs and time for both sides, but diagnostic exams also must be meaningful and appropriate. Quality of the results of diagnostic exams must be at an appropriate level.

Bellow will be presented thermovision as the potential new diagnostic method and approach. We will explain the benefits of thermovision diagnosis, but also it will be mentioned some specific obstacles that this method has. It will point to the possibilities of thermovision application as a diagnostic method that can give the key guide to further treatment of emergency patients. The implementation of thermovision in modern clinical practice does not require huge financial efforts for health institutions at various levels of health care. Since this is a non-invasive method, the patient is not exposed to any additional risks. Thermovision devices are extremely easy to handle with strong mobility, so this type of diagnosis is selected for more detailed further analysis which will be presented in the paper.

In this paper, all considerations related to the use of thermovision in orthopedic applications will be focus on the application related to the diagnosis of conditions associated with the knee joint.

THE MOST FREQUENTLY USED DIAGNOSTIC METHODS

Modern orthopedics use a number of known methods, their variations and mutual combining in modern diagnostics. Fundamentals of many of these methods are known several decades ago, but they are getting the whole new meaning using the ideas and modern approaches as results of new technical and technological breakthroughs. Most common diagnostic methods that are now applied worldwide in the context of diagnosing the state of the knee joint and in orthopedy at all are described below.

Radiography is method based on using X-rays for diagnostic approach. Recorded images obtained in this way shows the interior of the body in the shades of white and black colors (pure white color indicates a maximum absorbance). Calcium in the bones absorb the maximum amount of X-rays, so the bones appear white on image and that is the reason why X-rays is used primarily for the detection of fractures and deformities [1]. The main limitation in the application of conventional techniques of X-ray radiation for examination of internal structure in the organism are the difficulty or inability of a three-dimensional structure analysis, photographic film does not have a dynamic component and there are difficulties in the soft tissues of similar density diagnostic procedures [2].

Computer Tomography (CT) also use X-rays for imaging but the diagnostic procedures are improved by the progress of technology and especially by using of computer technologies. Tomography represents the imaging layer by layer. This method applies X-rays using a special circular technique [2]. Special apparatus (CT scanner) based on the mentioned technique create cross-sectional images of the body. Images are recorded by and within the computer which made possible to record a series of adjacent layers [3]. Whole process gets a dynamic component now, which allows to track various changes, such as changes in the soft tissues.

Magnetic Resonance Imaging (MRI) uses magnets and radio waves for the inspection of the body interior. MRI has gained tremendous popularity, it can be used for a various diagnostic procedures, from the ligament sprains to the discovery of a tumor. But MRI procedure can not be applied to all people because of the design of the apparatus which is based on the use of magnets. The magnetic resonance can not be applied to individuals who have already some foreign metal body in the organism (shrapnel, bullet) or with artificial limbs based on metal in the body (metal bars, rods), to persons who use electronic devices such as pacemakers and similar [4]. The representations obtained by magnetic resonance imaging have better quality than the same representations obtained using computer tomography [5].

Bone Scan is a diagnostic method intended for detecting bone diseases based on the transport of small amounts of radioactive material (radiotracer) in an organism. The aforementioned radioactive material is directly injected into a vein and then through the bloodstream spreads throughout the body, causing the corresponding small amount of radiation which can be detected. Detection was done with special devices that are equipped with special moving cameras which scan the whole organism and create diagnostic image [6]. Diagnostic procedure can last up to a few hours.

Thermovision as diagnostic method

Thermovision as the term refers to the recording of radiation intensity in the infrared part of the electromagnetic spectrum, and converting recorded data into a comprehensible image [7]. The main source of infrared radiation is essentially heat, characterized as heat radiation. Every object that has a temperature above absolute zero emits a certain amount of radiation in the infrared part of the electromagnetic spectrum [8]. Special equipment can detect infrared radiation and based on it a temperature image of the observed object can be formed. This process is called thermovision or infrared thermography [9]. On the obtained image, each pixel essentially represents one temperature characteristic of the observed object. Image created by the effect of heat radiation is called a thermogram [9].

Thermovision represents non-invasive method, especially popular in early detection of tumors. This diagnostic method can also be used for other diagnostic purposes, in the last decade there are large clinical studies covering the use of thermovision in other branches of medicine, such as orthopedics. When thermovision is used in medicine, it is recommended the use of appropriate scale for assessing the condition of subject. The mentioned scale is formed in relation to the observed temperature variation [10]. There is currently no defined universal scale, and it can vary in different cases, examinations, equipment. For example we could define that normal state is for temperature difference to 0.5 ^{O}C, monitoring is for 0.5 ^{O}C - 0.7 ^{O}C, prevention is for 0.8 ^{O}C - 1.0 ^{O}C, alert is for 1.1 ^{O}C - 1.5 ^{O}C and for temperature difference 1.6 ^{0}C and above we could claim that the patient is in very serious condition [10].

Some of the reasons that thermovision qualified as possible diagnostic method are: non-invasive method; patients do not feel any form of discomfort during the entire process; mobility; very short time need to complete whole diagnostic process; economic acceptability; ease of handling equipment; equipment has high degree of accuracy and reliability; point-and-shot approach (equipment is able to perform its own calibration and evaluation of environmental parameters). Also, thermovision is confirmed in practice, there are documented cases in the medical diagnosis where thermovision achieved concrete results in diagnostics of patients during the various procedures and treatments.

THERMOVISION APPLICATION ON THE REAL PATIENT WITH LEFT KNEE PROBLEM

During the thermal imaging, patient was in a sitting position while left knee joint was in the extension position. Left knee joint is imaged from three camera positions: from the left side (left view), from the right side (right view) and from the upper side of the knee (top view). Two sets of thermal images are done and every set has images from all mentioned camera positions.

Environmental parameters are detected automatically using software and algorithms embedded in the thermal imaging camera which is used for this thermal imaging. Values at the time of imaging were: emissivity 0.95, the reflected temperature 20.0 ^{O}C, the distance of the object of observation 1.0 m, the atmospheric temperature of 20.0 ^{O}C, the temperature of the external optics 20.0 ^{O}C, transmissivity of the external optics 1.0.

On the original thermal images captured with thermal imaging camera and before any further analysis and processing of images and data, temperature anomalies could be spoted in a region of left knee joint. Those temperature anomalies were presented on images with combination of white and pale yellow color. These findings were the first indication during diagnostic process that there is certain knee problem and that thermal images should be further analyzed.

In order to confirm previous findings, thermal images are processed using specialized software for thermal images processing. In the analysis of the thermographic images, a specific range of colors (Gray and Medical pallets of colors) were used in order to improve the display quality and the point out certain regions which have identified as interesting by direct observation. Also, specialized set of algorithms is used for providing a clear and sharp images with a satisfactory level of details.

After previous initial processing of thermal images, methods of software isothermal display are applied. Software isothermal display implies the use of a contrasting color on all points that have a temperature above, below or between the temperature levels defined by the user, which in essence represent the specific values of the alarm temperature. In this case, alarm temperature is set on 35 ^{O}C. This value is taken upon detecting that the normal states on thermal images are read up to the upper limit value of 35 degrees Celsius, and the alarm is set to a value greater than the above mentioned temperature.

As mentioned above, for the analysis and verification of results three different thermal imaging footage, taken from different angles, are used, which leaves enough space for proper interpretation of results. All thermal imaging recordings are made in the same conditions, so the impact of the external environment on the recording results on all images are identical. On all thermal images are confirmed mentioned temperature anomalies in left knee joint area, discovered by preliminary observations.

Looking at the confirmed temperature anomaly reveals that the source of the events (focal point) is located in the central part of the left knee joint and then further events are transferred to the right, toward the internal (inner) part of the leg. This gives us the localization, but it still can not be claimed with absolute certainty what the seriousness of the situation that occurred.

The severity of the condition will assess by further analysis of thermal images using calculated temperature difference.

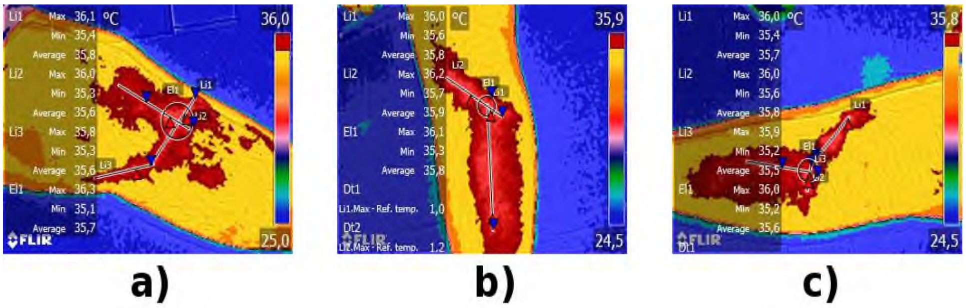

Figure 1. Processed thermal images with actual measurements

As shown previously, currently in use are thermal images with Medical palette of colors with contrasting display achieved with the help of an alarm designed for temperatures over 35 ^{O}C. According to alarm temperature, the reference temperature will be set on the same value which is precisely the temperature of 35 ^{O}C.

In accordance with the available tools for measuring the temperature within the software tool for the transformation of thermal imaging, two types of temperature measurements are performed: linear temperature measurements and circular (elliptical) temperature measurements. Regardless of the type of measurement, three characteristic temperatures are detected for each executed measurement: the maximum temperature, the minimum temperature and the average temperature of measurement.

For each measurement, the temperature difference is calculated as

$$\Delta_i = T_{i_{max}} - T_{ref}$$

where is i - label of the current measurement, Δ_i- calculated temperature difference of the i-th measurement, $T_{i_{max}}$- maximum temperature of the i-th measurement, T_{ref}- reference temperature and wherein $T_{ref} = 35$ ^{O}C. Measured and calculated temperature values for thermal images shown at figure 1 are presented in table 1.

Table 1. Measured and calculated temperatures for thermal images on figure 1

Label	T_{max}	T_{min}	T_{avg}	ΔT
Fig. 1 a) - Li1	36.1 ^{O}C	35.4 ^{O}C	35.8 ^{O}C	1.1 ^{O}C
Fig. 1 a) - Li2	36.0 ^{O}C	35.3 ^{O}C	35.6 ^{O}C	1.0 ^{O}C
Fig. 1 a) - Li3	35.8 ^{O}C	35.3 ^{O}C	35.6 ^{O}C	0.8 ^{O}C
Fig. 1 a) - El1	36.3 ^{O}C	35.1 ^{O}C	35.7 ^{O}C	1.3 ^{O}C
Fig. 1 b) - Li1	36.0 ^{O}C	35.6 ^{O}C	35.8 ^{O}C	1.0 ^{O}C
Fig. 1 b) - Li2	36.2 ^{O}C	35.7 ^{O}C	35.9 ^{O}C	1.2 ^{O}C
Fig. 1 b) - El1	36.1 ^{O}C	35.3 ^{O}C	35.8 ^{O}C	1.1 ^{O}C
Fig. 1 c) - Li1	36.0 ^{O}C	35.4 ^{O}C	35.7 ^{O}C	1.0 ^{O}C
Fig. 1 c) - Li2	36.0 ^{O}C	35.6 ^{O}C	35.8 ^{O}C	1.0 ^{O}C
Fig. 1 c) - Li3	35.9 ^{O}C	35.2 ^{O}C	35.5 ^{O}C	0.9 ^{O}C
Fig. 1 c) - El1	36.0 ^{O}C	35.2 ^{O}C	35.6 ^{O}C	1.0 ^{O}C

After examining obtained results from the table, we can find the maximum temperature difference which is a result of the subject measurement and calculation. We note that the realized $\Delta T_{max} = 1.3$ for the case of measurements El1 (circularly temperature measurement) for thermal image referred as a) in figure 1. That maximum value of the temperature difference will be used in the further analysis.

By comparing the results obtained for ΔT_{max} with the scale mentioned before and according to [10], we conclude that the result fits exactly in the range of 1.1 ^{O}C - 1.5 ^{O}C, which is in given scale claimed as a state of alarm. This indicating that a patient is in condition that can cause further consequences that may remain permanent for patient.

Based on the data obtained, we are now able to complete the "thermovision findings" for the patient, because now all findings are based on facts which are product of the thermal images analysis instead of direct observations. According to that we could say that there is a serious condition in the current area of the left knee joint and it is noted that affected the central part of the knee joint and that this region continues to expand towards the inner side of the knee joint.

CONCLUSION

The resultant synthesized data can give a doctor specialist confirmations about the conclusions adopted on the basis of direct observation and review the situation of the patient. Also, they can provide the necessary guidelines when patients are sent for further diagnosis and observation, define the urgency of certain actions, procedures.

Unfortunately, thermovision for now gives only a partial picture of medical state and offers limited power of observation. Using thermovision we can not get a realistic representation of the interior and the state of organs. This type of diagnostic can not give a complete three-dimensional display, but can provide significant guidance during the transition to the same using other diagnostic methods, since it can take important actions in terms of localization and assessment of patients, especially in those cases where the patient is unable to or simply does not know how to describe the symptoms, or the symptoms are hidden in some other symptoms.

As is evident from the results, thermovision can be widely applied in the field of medical diagnostics. In the specific case, it is evident that the use of thermovision can get a better insight into the seriousness of the current patient state. Also, we get a clearer picture and insights into symptoms and descriptions of the patient state. From the foregoing and shown it can be concluded that the thermovision in triage departments and services in conjunction with the work of specialists can give a new dimension in understanding the condition of patients.

As a basic lack of thermovision method is the fact that it achieves insight only into the existence of the problem and hotspots, while the view inside the body of the patient with this method, unfortunately, can not be achieved, so additionally method of medical diagnostics must be applied. Thermovision is carried out only in two-dimensional space without possibility of a three-dimensional model generation that would provide better insight into the current and general condition of the patient that some other methods of medical diagnostics are providing such as for example magnetic resonance imaging.

REFERENCES

1. X-Rays, MedlinePlus.gov, MedlinePlus, U.S. Department of Health and Human Services, National Institutes of Health, U.S. National Library of Medicine, Bethesda, Maryland, USA, 2016.
2. Dejan Popović, Mirjana Popović, Biomedicinska instrumentacija i merenja, Nauka, Belgrade, Serbia, 1997.
3. CT Scans, MedlinePlus.gov, MedlinePlus, U.S. Department of Health and Human Services, National Institutes of Health, U.S. National Library of Medicine, Bethesda, Maryland, USA, 2016.
4. MRI Scans, MedlinePlus.gov, MedlinePlus, U.S. Department of Health and Human Services, National Institutes of Health, U.S. National Library of Medicine, Bethesda, Maryland, USA, 2016.
5. Igor Borić, Procjena i klasifikacija početnog oštećenja hrskavice koljena magnetskom rezonancijom, PhD thesis, School of Medicine, University of Zagreb, Zagreb, Croatia, 2011.
6. Bone scan, MedlinePlus.gov, MedlinePlus, U.S. Department of Health and Human Services, National Institutes of Health, U.S. National Library of Medicine, Bethesda, Maryland, USA, 2016.
7. Thermal imaging for security & surveillance, FLIR Systems Inc., Wilsonville, Oregon, USA, 2014.
8. Thermal imaging guidebook for building and renewable energy applications, FLIR Systems Inc., Wilsonville, Oregon, USA, 2014.
9. Zoran Stević, Mirjana Rajčić-Vujasinović, Dejan Antić, Primena termovizije, Technical faculty in Bor, Univeristy of Belgrade, Bor, Serbia, 2008.
10. Marins, J.C.B.; Fernández-Cuevas, I.; Arnaiz-Lastras, J.; Fernandes, A.A. y Sillero-Quintana, M. (2015). Aplicaciones de la termografía infrarroja en el deporte. Una revisión / Applications of Infrared Thermography in Sports. A Review. Revista Internacional de Medicina y Ciencias de la Actividad Física y el Deporte vol. 15 (60) pp. 805-824

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INFLUENCE CIVILIAN AIR TRAFFIC ATMOSPHERE TIMOCKE KRAJINE II

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ABSTRACT

Since 2005, when they carried out the first survey until 2016, the impact of subsonic aircraft (that belongs to the civil aviation) on the chemical composition of the atmosphere above the Timok region is large, and is directly dependent on the number of overflights of aircraft, altitude, exhaust-combusted-gas emissions as, and the background of atmospheric concentrations of sulfur, chlorine, aerosols and other chemical compounds in industrial installations in that territory. In the last eleven years in the airspace above the Timok region saw a sharp rise in air traffic. According to the present projected fuel consumption, we can see that the past 20 years, fuel consumption increased by 75% with an estimate that for the next 30 years, the increase will be for 100-200%. Alone consumption of fossil fuel in the air transport amounts to 3% of the total world consumption of fuel, while the total fuel consumption of the aircraft 99% of the fuel consumption related to traffic aviation.

Subsonic flights take place in the upper troposphere (below 11km) or in part, and in the lower stratosphere near the tropopause (where subsonic aircraft consume 44% of the total flight time per year) to depend on, and the latitude and season. The retention time of the combustion products emitted jet fuel in this layer of the atmosphere (until the moment of exchange between the stratospheric-tropospheric layer) is several months.

Key words: subsonic aviation, troposphere, stratosphere.

INTRODUCTION

Reduction of oxygen in the upper atmosphere (flights 11km below) is due to the possible number of subsonic aircraft. The lower layer of the stratosphere, where the combustion products are entered directly aviation fuel, changes in the chemical and dynamic mode atmosphere. Subsonic aviation above Timok region (East corridor) increases the concentration of NOx in the above tropospheric heights of 3-30%, the water vapor concentration of 0.03%, 3% for SOx, soot of 3%, in relation to the atmosphere without stop, provided all planes flying below the tropopause. The retention time of a concentration of the chemical elements of sulfur dioxide and sulfate mixture was 2-6 days, depending on the wind in the upper troposphere, can be moved up to 4000km of their springs, which are the factors and contamination on the part of the territory overflown without the air (air -corridor). Transportation, deposition and transformation of the pollutants in the atmosphere-lower layers of the troposphere vary according to geophysical and geochemical characteristics of the territory, over which these processes take place. First of all, it should be borne in mind big industrial plants that are dangerous, tocsic- carcinogen. In this regard, the direction (Eastern Corridor) is Bor. As localities and influence in the last year has a tendency of reducing air pollution, improving environmental protection, which is only a couple of years ago it was significant air polluters, including spearheaded the smelter unit and sulfuric acid plant. Annually it is over 300t 200.000t sulfur and arsenic. Sulfur, arsenic, mercury, cadmium, and other heavy metals, were constantly present in the air at high concentration, even when the smelter and sulfuric acid do not work at full capacity. As an inevitable consequence of the present permanent state of emergency in terms of air quality, there are dangerous respiratory diseases in humans, and targeted primarily at children. When working factory sulfuric acid reduced capacity, reduced by the use of waste gases smelter, which leads to increased emissions of sulfur dioxide, arsenic and heavy metals, which in the last two years, overcome by building a new smelter and sulfuric acid. This industry has its own peculiarities, especially on additional emissions in the lower layer of the troposphere, so that the above-mentioned location occur additional environmental burdens on the environment, the local (0,1-5km) and shorter regional (5-100km) a complex process of deposition, and transformation of pollutants, depending on the type and height as are omitted, leaving the greatest impact in the area, just in the local and regional authorities.

CONCLUSION

Surface area is 7131km² Timok region, wherein one part of its air, at a height of 8-10km converted to civil air corridor (East corridor). Direction corridor above the settlement town of Bor and also above the industrial zone. Mining and metallurgy have contaminated the air duct, plot a number of harmful substances. The contaminated air is supplied to the slow growth and development in children, reduces the resistance to infections, and affect the onset of diseases of the internal organs. Employed in the copper metallurgy, they are exposed to high concentrations of sulfur dioxide, arsenic, lead, copper, cadmium and other heavy metals. Medical research in the population Bor, showed significantly increased amounts of arsenic in blood and pieces of lead in the blood and urine ... The results show that the mortality rate was analyzed by age groups, in people over 40 years of age, the greater Bor, but in the Timok region. This indicates the carcinogenic substances in the environment Bor.

The importance of clean air for living and working population in the region does not need further comment. The very air ionization is of great importance (it should be as many negative ions in the air), for both work and life, and can rightly be said that the negative joni- natural vitamins. A constant concentration of pollution in the environment is dominated by this distance, permanently reduces the amount of oxygen, as well as the creation of positive ions in the air. In a couple of years behind us significantly reduced the impact of melting aggregates, or as a problem occurs, the impact of increased air traffic, (a large number of aircraft overflights) in the corridor above this part of the Timok Krajina. That the air transport and combustion products, relevant to environmental pollution over Bor, as well as the entire territory of the Timok region, according to research conducted in 2005 and 2016. Using (Eastern Corridor) over the territory of the Timok Krajina, for a one-year period, is spent 350.000t air (in this context, and oxygen) which is equal to the quantity that is sufficient for wildlife in this area over the next 8 months. Elements of impact of the civil air transportation (Eastern corridor) to atmosphere above Timok region in 2005 are shown in Tables 1 and 2 of the 2016 in the tables 3 and 4.

Table 1. Daily activity of air traffic in the (Eastern Corridor) 2005

Number of aircraft overflights	Time of flight (min.)	Fuel consumption (t)
150	4	0,8

Table 2. Annual Activity aircraft overflights in (Eastern Corridor) 2005

Number of aircraft overflights	Retention Time (h)	Fuel consumption (t)
54000	3600	292

For eleven years (2016), all parameters were significantly increased. Elements of impact of the civil air transportation (East corridor) to atmosphere above Timok region in 2016 are shown in Tables 3 and 4.

Table 3. Daily activity of air traffic in the (Eastern Corridor) 2016

Number of aircraft overflights	Weather flypast in (min.)	Fuel consumption (t)
648	4	3,44

Table 4. Annual Activity aircraft overflights in (Eastern Corridor) 2016

Number of aircraft overflights	Retention Time (h)	Fuel consumption (t)
233.280	15552	1255

REFERENCES

1. The impact of civil aviation on the atmosphere of the Timok Krajina SRTOR / Žan Disterlo, 2005.
2. Ecological consequences of the NATO war in Yugoslavia ECO Center Belgrade, 2000.

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ASPECTS REGARDING THE DEVELOPMENT OF ECOTOURISM IN THE SEMENIC - CARAŞ GORGES NATIONAL PARK, ROMANIA

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ABSTRACT

Ecotourism is the answer given by people loving to spend their free time in an unaltered natural environment to those seeking urban areas providing multiple services.

The existence of protected areas makes it possible to preserve authenticity and develop controlled and environmental friendly tourist activities. Hiking and speleology are forms of tourism promoted in such areas.

In Romania, there is a series of different protection regime areas, one of them being the Semenic-Caraş Gorges National Park. The management of the park is trying hard to develop ecotourism.

Key words: protected area, tourist resources, ecotourism.

INTRODUCTION

A protected area is a „land, aquatic and/or subterranean area with an established legal perimeter and a special protection and conservation regime, where there are species of wild plants and animals, bio-geographical, landscape, geological, paleontological, speleological elements and formations, with remarkable ecologic, scientific and cultural value”[1].

Generally, protected areas are:

- scientific reserves;
- national parks;
- monuments of nature;
- natural parks;
- natural reserves;
- biosphere reserves;
- wetlands of international importance;
- natural sites of the universal natural heritage;
- special conservation areas;
- special protection aquatic and fauna areas.

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[1] Burlacu, G.(coord.), Mediul înconjurător, termeni şi expresii uzuale (The environment, terms and usual expressions), Paideia Publishing House, Bucharest, 2003

The IUCN (International Union for Conservation of Nature) classification system that is based on the main management objective of the area supports the following categories of protected areas:

- Category Ia – strict nature reserve;
- Category Ib – wilderness area;
- Category II – national park;
- Category III - natural monument or feature;
- Category IV – habitat/species management area;
- Category V – protected landscape/seascape;
- Category VI – protected area with sustainable use of natural resources

In Romania, national parks account for 316.758 ha and are spread all over the country.

Table 1. National Parks in Romania

No.	**Name of park**	**Area (ha)**	**Webpage**
1.	Ceahlău	8396	http://www.ceahlaupark.ro/
2.	Bicaz – Hăşmaş Gorges	6575	http://www.cheilebicazului-hasmas.ro
3.	Retezat	38047	http://www.retezat.ro
4.	Buila Vâturariţa	4186	http://www.buila.ro
5.	Cozia	17100	http://www.cozia.ro
6.	Nera - Beuşniţa Gorges	36758	http://www.cheilenerei-beusnita.ro
7.	Călimani	24041	http://www.calimani.ro
8.	Jiu Gorges	11127	http://www.defileuljiului.ro
9.	Măcin Mountains	11321	http://www.parcmacin.ro
10.	Rodnei Mountains	46599	http://www.parcrodna.ro
11.	Piatra Craiului	14733	http://www.pcrai.ro
12.	Semenic - Caraş Gorges	36664	http://www.pnscc.ro
13.	Cerna – Domogled Valley	61211	http://www.domogled-cerna.ro
14.	Total	316758	

Source: https://ro.wikipedia.org/wiki/Lista_parcurilor_nationale_si_naturale_din_România

Alongside these national parks there is a series of other protected areas included in different categories, and among these the Danube Delta is included in the world heritage list UNESCO.

Ecotourism means a responsible travel within a protected area that protects the environment and positively influences the inhabitants' income. Ecotourism activities include watching, protecting and knowledge (bird watching, spotting wildlife, botanical trips, trekking, camping, diving, speleology, archaeology, photo safari, landscape painting).

Hiking is the most recommended way of travel within the protected areas, but one can also use specially trained animals (horses, elephants, camels), traditional means of transport (carts, sleighs), hot-air balloons, bicycles, boats, cars (in allowed areas).

The development of ecotourism gives the hope of preserving certain tourist resources for the future generations as well.

SEMENIC-CARAŞ GORGES NATIONAL PARK

The Semenic-Caraş Gorges National Park lies in the south-west part of Romania, in Caraş- Severin County, under the administration of Reşiţa, Caraşova, Goruia, Anina, Bozovici, Prigor, Teregova and Văliug. This park is located in the mountain areas of Anina and Semenic that are part of the Meridional Carpathians and has altitudes between 200 and 1447 meters, Gozna Peak reaching the highest altitude. Caraşova, Anina, Văliug, Gârlişte, Cuptoare, Gărâna, Borlovenii Vechi, Bozovici, Iabalcea, Reşiţa are the access localities to the Semenic-Caraş Gorges National Park.

In 1955 they declared the Mixed Reserve Caraş Gorges, in 1994 the Semenic-Caraş Gorges National Park was confirmed by Decision no. 8 of the Caraş Severin County Council, and it was reconfirmed by Law no. 5 in 2000.

The following reserves are found inside this protected area:

- Caraş Gorges;
- Gârlişte Gorges;
- Buhui-Mărghitaş;
- Caraş Springs;
- Nera's Springs;
- Bârzăviţa;
- Groposu;
- Buhui Cave;
- Comarnic Cave;
- Popovăţ Cave.

Inside the Semenic-Caraş Gorges National Park there are strict protection areas, as well as total protection areas.

Table 2. Areas of the Semenic-Caraş Gorges National Park

No.	Name of area	Protection regime	Area (ha)	Percentage in entire park (%)
1.	Răsuflătoarei Cave	strict	1,1	0,003
2.	Nera's Springs	strict	5012,32	13,67
3.	Caraş Gorges - upstream	strict	246,74	0,67
4.	Caraş Gorges - upstream	strict	282,29	0,77
5.	Caraş Gorges	total	2988,67	8,15
6.	Gârliştei Gorges	total	582,18	1,59
7.	Caraş Springs	total	1384,06	3,77
8.	Buhui	total	217,64	0,59
9.	Turbării	total	283,82	0,77
10.	Comarnic Cave	total	26,9	0,73
11.	Popovăţ Cave	total	4,5	0,01
12.	Exploratorii'85 Cave	total	15	0,04
13.	Semenic - Caraş Gorges National Park	-	36664	100

Source: http://pnscc.ro/ processed data

Out of this park's total area, 30,13% has strict and total protection regime, certain activities being forbidden.

The relief is mainly mountainous, in the west we see Anina Mountains, while in the east Semenic Mountains.

Here we find depressions, valleys, gorges, and karst formations. The caves and abysses are grouped in nine speleological basins, and the most popular caves are Comarnic, Popovăţ, Răsuflătoarea, Buhui, Exploratorii 85.

Table 3. Number of speleological formations

No.	Speleological basin	No. of caves	No. of abysses
1.	Miniş Valley	3	0
2.	Gârlişte	77	7
3.	Buhui - Luca	89	14
4.	Left versant of Caraş Gorges	123	23
5.	Right versant of Caraş Gorges	136	12
6.	Iabalcei Plateau	3	25
7.	Comarnic - Topliţa	85	14
8.	Râul Mare	58	132
9.	Nermet	0	2
10.	Total	574	229

Source: http://pnscc.ro/

The park has a rich hydrograph network, both on the surface and underground. The rivers Timiş, Bârzava and Nera flow from the Semenic Mountains, and the Caraş River flows from Anina Mountains. The springs around the park are Caraş Spring, Izvorul Mare from Grohotiş, Certeje, de sub Viaduct, Trei Izvoare, Sodol.

The climate is moderate continental temperate with Mediterranean influences, which brings early springs.

Rich vegetation has developed due to the altitude and climate, 88% of the analysed area being wooded. Specialists have identified more than 1.200 plant species, 30 of which being protected species. Also, the fauna is adapted to conditions of relief, climate and vegetation with 691 animal species living here, 34 of which being under strict protection.

The park's tourist attractions are especially natural, but there are also anthropogenic resources.

Table 4. Tourist attractions of the Semenic - Caraş Gorges National Park

No.	Name of tourist resource	Characteristics
1.	Virgin beechwood Nera's Springs	About 5000 ha; The beechwood is over 300 years old;
2.	Caraş Gorges	Length 19km, depth 200m ; Limestone walls;
3.	Gârliştei Gorges	Length 9 km; Depth between 100 and 200m;
4.	Comarnic Cave	Remarkable underground landscapes; Underground river;
5.	Poiana Gropii Abyss	The deepest in Banat; Located near Văliug;
6.	Popovăţ Cave	Lenth 1121m
7.	Buhui Lake	Built in 1908; Area of 1,6km^2; Depth 27m;
8.	Grat Fortress	Medieval fortress- ruins; Legend.

Besides the tourist resources, the annual events and the traditions from Caraşova and Gărâna attract tourists. The development of tourism in this area, where permitted, is possible and there are ongoing endeavours to that effect.

ASPECTS REGARDING ECOTOURISM IN THE SEMENIC-CARAŞ GORGES NATIONAL PARK

The accommodation and food facilities from the localities situated within the protected area or its margins are diversified and meet the needs of tourists. Such facilities can be found in Reşiţa, Caraşova, Anina, Văliug, Gărâna, Crivaia and Semenic.

A series of visiting rules have been established for the conservation of this park:

- Any visit supposes an entry fee;
- Camping can be done only inside permitted and marked areas;
- Lighting fires is prohibited;
- No competitions or events can be organized;
- Any leftovers are forbidden;
- Deviation from marked tourist tracks is forbidden;
- Using any kind of chemical products is forbidden;
- Collecting plants or fauna is forbidden;
- Disturbing the calmness of the park is forbidden;
- Using motor vehicles or bicycles is allowed only on certain trails;
- Access of accompanying dogs is allowed only in a leash and on marked trails.

Tourist activities that are currently carried out in the protected area are:

- Hiking;
- Speleology;
- Climbing;
- Flora and fauna watching;
- Practicing winter sports;
- Developing agritourism in the neighbouring areas.

Several tourist trails were marked for hiking, one having a high degree of difficulty where tourists need to have a good physical condition.

Table 5. Tourist trails in the Semenic- Caraş Gorges National Park

No. of trail	Name of trail	Length	Difficulty
1.	Secu Lake - Borlovenii Vechi	58,4 km	high
2.	Reşiţa – Gura Golumbului Lake	37 km	medium
3.	Comarnic Cave - Baia Vulturilor	9 km	medium
4.	Caraşova – Gârlişte	3,5 km	easy
5.	Dealul Certej – Cioaca Mare	1,3 km	easy
6.	Crucea Iabalcei - Prolaz	3 km	easy
7.	Caraşova – Comarnic Cave	9 km	easy
8.	Anina – Gârlişte	12 km	easy
9.	Cuptoare - Semenic	12,5 km	medium

Source: http://pnscc.ro/trasee-turistice/

Trails no. 4, 6, 7 and 8 are accessible during winter as well; the equipment for all trails is a normal one, adequate for hiking in the mountains.

Figure 1. Semenic - Caraş Gorges National Park Map – tourist trails
Source: http://pnscc.ro/harta-parcului/

A management plan regarding the development of ecotourism in the Semenic-Caraş Gorges National Park would require:

- Constructing ecological parking places in the access localities;
- Erecting observation towers where the access is permitted;
- Constructing belvedere places;
- Identifying traditional houses and using them as pensions;
- Setting up camping places;
- Setting up ecological toilettes;
- Marking and maintaining toilettes and tourist trails;
- Mounting information signs;
- Preserving traditions and crafts;
- Making souvenirs from stone, wood, wool;
- Instructing locals for carrying out ecotourism activities;
- Proper setting up of some caves;
- Elaborating, together with travel agencies, accommodation and food facilities, programmes for thematic tourism.

For the time being, the development of ecotourism is at an incipient stage, and the efforts of the park's administration, local authorities, locals, NGOs must continue. All those involved must be aware of the importance of the development of ecotourism in this area.

CONCLUSIONS

Ecotourism can be considered an opportunity for nature, locals and investors. One of the national parks of Romania is the Semenic - Caraş Gorges National Park.

Currently, authorities are preoccupied with developing ecotourism in this protected area, but they lack a more decisive involvement. Accessing European funds would be the necessary incentive for the development of ecotourism in this park.

REFERENCES

1. Burlacu, G.(coord.), Mediul înconjurător, termeni şi expresii uzuale (The environment, terms and usual expressions), Paideia Publishing House, Bucharest, 2008
2. https://ro.wikipedia.org/wiki/Lista_parcurilor_nationale_si_naturale_din_România
3. http://pnscc.ro/

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INOVATION AND SUSTAINABLE DEVELOPMENT

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ABSTRACT

Innovations are the driving force of the technological development of steel production. The most used material is steel. From the beginning of the iron and steel production in the direct procedures in »simple« furnaces till the most modern procedures in oxygen converters or EAF, a lot of innovations and development work materialized along the way. At the production of steel, slags are formed, mostly used as a secondary raw material. At the production of liquid steel (converter, EAF) we use different procedures of secondary refining of liquid. Innovative procedures of refining processes enable the development of new steel qualities and with this the competitive position of companies on the global market. At every new technological procedure different slag is formed, which has to be suitably processed in order to use it as a secondary raw material.

INTRODUCTION

Research work and cooperation between researchers on faculties and technologists in steel plants at the development of technology of the production of alloyed steels was reported at many scientific and technical conferences. Processing of EAF refining slags mainly with respect to the Zinc distribution in EAF dust was discussed. Slags in EAF dust can be used as a secondary raw material[1 - 6] .

AOD SLAGS

Manufacturing of the AOD converter for special stainless steels was planned for years and now became reality[7]. During preparation stage of the intended investment, research work of the slags originating from the production in AOD (Argon Oxygen Decarburisation) converter in order to recognise the properties of slags and also influences on the environment, was done[8].

In Tables 1, 2 and 3 the composition of slags, originating at different technological phases of secondary refining after oxidation of carbon, reduction of slag and desulphurization of liquid phase is presented.

Table 1. Composition of slags after the oxidation of carbon in mass%.

CaO	MgO	MnO	FeO	Cr_2O_3	SiO_2	Al_2O_3
35/55	0.8/3.5	3.8/6.4	6.8/8.4	21/40	5.1/10.7	0.2/0.5

Table 2. Composition of slags after reduction with silicon and/or aluminium.

CaO	MgO	MnO	FeO	Cr_2O_3	SiO_2	Al_2O_3
50/55	1.5/3.7	1.8/2.9	0.3/0.5	1.9/3.1	25/35	0.0/1.7

Table 3. Composition of slags after desulphurization.

CaO	MgO	MnO	FeO	Cr_2O_3	SiO_2	Al_2O_3	CaF_2
60/70	0.7/2.2	0.3/1,1	0.2/0.6	0.5/1,5	12/20	0.2/0.4	6/10

Slag composition after oxidation of carbon, reduction phase and desuplphurization can be presented in ternary diagrams: $CaO–SiO_2–Cr_2O_3$, $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2-CaF_2$, respectively[9].

SLAGS FROM ALLOYED STEEL PRODUCTION AND CUPOLA SLAGS

At the production of different types of alloyed steels various slags are formed containing calcium silicates, also calcium aluminates and free calcium oxide. In foundries during melting in cupola furnace acid slag and foundry sand is formed. The composition of boundary phase at the contact between refining slag and slag from cupola furnace was investigated.

Figure 1, depicts glass phase structure of cupola slag. In Figure 2 shows microstructure at the phase boundary between cupola slag and slag from alloyed steel production. The phase boundary is void from glass phase structure and after heating at the 1250°C new phases are formed. Their composition can be described by using microanalysis and multi-phase diagrams and will be presented at the presentation. Reusable foundry sand starts to sinter at the 1250°C and is depicted in Figure 3 after sintering.

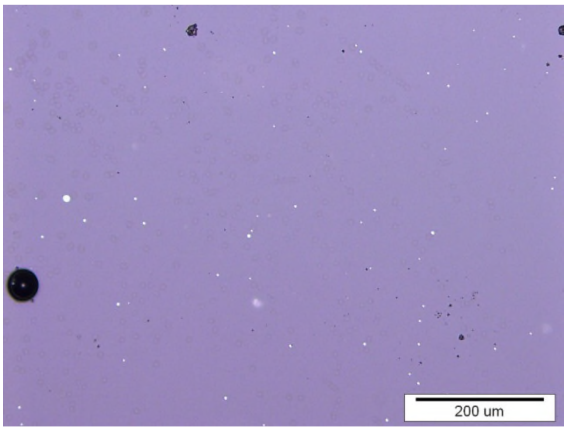

Figure 1. Glass phase structure of cupola slag

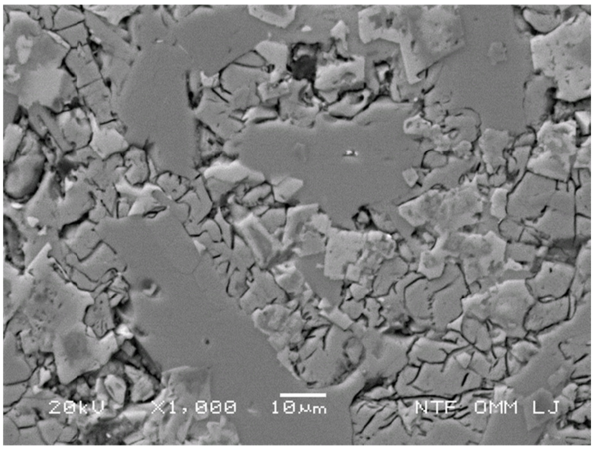

Figure 2. Microstructure of the phase boundary after sintering on 1250°C.

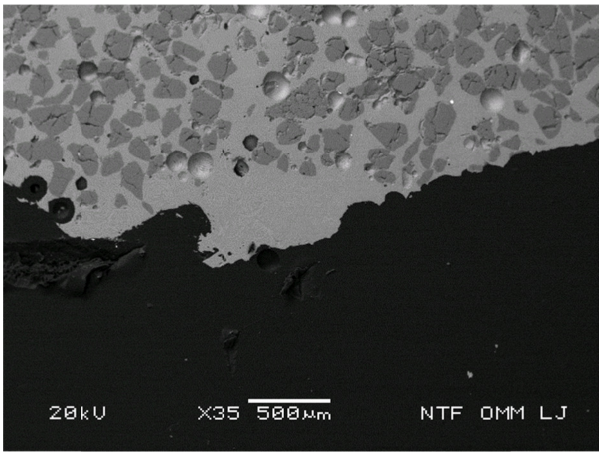

Figure 3. Microstructure of the sintered foundry sand.

CONCLUSION

It is important that during the planning stage of new innovative technologies, where during the production phase various by-products are formed, the research work and plans of reusability of by-products as a secondary material are taking into account. In this way the sustainable production will be inevitably part of innovative technologies.

REFERENCES

1. J.Lamut,A. Rozman, M. Debelak, B. Lamut. M. Knap: Phase composition and recycling of by-products from steel production. Proceedings, Ecological Truth. Kopaonik, 17 – 20. 6. 2015, P. 145/150.
2. J. Lamut in et al.: Phase composition of dust particles: 6. Simpozium »reciklažne tehnologije i održivi razvoj«,.Zbornik radova,.Soko Banja 18. – 21. september 2011, S. 48/53
3. A. Rozman, J. Lamut et al.:¸Stabilization of Ladle Refinings Slags with Borax. Proceedings of the European Slag Conference,19th - 21st September 2007, Luxembourg.
4. J. Lamut, A. Rozman, M. Knap, M. Debelak, B. Lamut,: By-product of steel production, 7. SRTOR, Soko Banja, 5. – 7. 9. 2012, S. 319/325.
5. E. Hristova, M. Knap, M. Debelak' A. Rozman, J. Lamut : Phase composition of by-products from steel making. VIIth International metallurgical congress, Ohrid, 9. – 12. 6. 2016.
6. B. Lamut: Termična priprava EOP prahu: Magistrsko delo, UL NTF Oddelek za materiale in metalurgijo, Ljubljana 2010.
7. Revija skupine SIJ – Slovenska industrija jekla, št. 2/2017
8. D. Lesjak: Izdelava nerjavnih jekel: Diplomska naloga. UL FNT- Montanistika 1990.
9. Slag Atlas: Verlag Stahleisen GmbH, Düsseldorf 1995.

URBAN ECOLOGY AND SUSTAINABLE DEVELOPMENT OF CITIES

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ABSTRACT

Today`s lifestyle is primarily an urban style. It is lifestyle of an urban consumer household that could not exist without the private market and the public infrastructure. Historically the consumer household is a very yang phenomenon. It only started to gain acceptance with a large proportion of the population in the middle of the 19th century when urban industrialization began. Cities should trigger people to be creative and will in turn be altered creative environments. It is necessary to establish a process for engaging participation by the general population in setting goals and strategies for a public environmental policy. When designing and planning of urban space is necessary to return to the fundamental values that dictate that urban development should be aligned with the needs of the population. One of the most important needs is just the man for his own existence must learn to live in harmony with nature. The basic hypothesis is that the urban ecology an integral part of daily management of the city, but is also a social task as far as the way of life urban residents. The purpose and goal of the work is to highlight the issues that our present way of life imposes, and this is to develop cities without sufficient attention to the quality of life that is through the application of urban ecology.

Key words: urban ecology, sustainable development, sustainable cities, urban culture.

INTRODUCTION

Modern study of the ecology of the city a few are dedicated to the city as an ecosystem and more individual problems, such as pollution and destruction of natural species and endangering human life (Šimunović, 2007: 170). Due to the high population density and the production of natural subsystems in the city were destroyed or modified, so the 90s began the idea of urban sustainability development as a new environmentally ethical-term or continuous process that reflects the ratio of a dialectic between the economy, society, politics and the environment (Pugh, 2000). Thus, the European Economic Commission in 1989 formally adopted sustainable development as a guiding principle for all relevant activities that this type of development is seen as "a process or a program of economic restructuring, social and technical relations in order to protect nature and the environment to use present and future generations (Črnjar, 2009: 79). Since important documents related to the Sustainable development also includes the Agenda 21 (http://www.sustainabledevelopment.un.org) which is interpreted as population, technology and consumption of the primary driving forces cause changes in the environment and suggests how to reduce inefficient and wasteful consumption some parts of the world (Peračković, 2013). So even though people are part of the problem, they shared Forces can be a solution of the same problem because citizens make up "construction material" sustainable directory (Adormbent, 1998). Urban ecology can be viewed globally, comparing activities by country of the world (Tao, Grimm, 2015) or to explore the area of a city, which an attempt in this paper. Urban ecology enters the human ecology, and deals with the built Environmental and undeveloped space. This includes the maintenance, protection and preservation of the built and undeveloped environment from adverse effects resulting from or may be formed by building (Morsan et al., 2007: 456). Urban spaces for its inhabitants serve as a place to consolidate all functions related to human needs, housing, provision of means of subsistence, social utility and interaction (Davies et al., 2011). Lately it seems that man forgets that the city has to create on a human scale, but in harmony with nature. S the advent of industrialization, cities have been transformed into a place where nature is exaggerated exploits. Through the work aims to show a causal link urban ecology and urbanization, or relationship between urban planning and the environment according to the principles of sustainable development.

Urban ecology means to interfere with the relationship of spatial (physical) and environmental, which is a fundamental preoccupation of urban ecology.

URBAN ECOLOGY AS THE INTERDISCIPLINARY AND APPLIED SCIENCE DISCIPLINE ABOUT ENVIRONMENT

For any one person, the ecological environment is very important, it can provide for human survival and development of material basis and the necessary variety of other conditions. Inappropriate if the ecological environment, human beings cannot survive and develop. We can say that human existence and development, are dependent on a suitable environment. However, our economic and social development has already caused damage to the environment, but also gives us a threat to sustainable development. Our ecological environment of the city a very important part of its development and changes in the same human survival and development have a huge impact. The concept of eco-city came into being, it is affordable in the city within the ecological, the use of the principle of sustainable development and the basic principles of ecological economics, urban economic way of promoting change from the point of view, in order to improve the city environmental quality for the purpose of seizing the city's main line of the industrial structure adjustment of the layout to play the city's resources, through overall planning and promote the comprehensive development of the city's ability to achieve sustainable socio-economic development. In this paper, the construction of ecological city and sustainable development were studied.

Ecology, a branch of biological sciences, strives to understand relationships of interdependence in the natural world, and (while not at heart activist) at times to devise strategies for their preservation. As such, of course, it informs environmental regulators and thereby places some constraints on development activity. Urban planning, on the other hand, exists to provide analysis in the service of action, and its principal concerns historically have been economic to pursue and facilitate development while striving as well to preserve and enhance the market value of existing property investments. Planners have other concerns as well, to be sure, such as improved public health, social equity, and an attractive public realm -- all of which have vital ecological dimensions. So one would be hard-pressed indeed to find a planner who disagreed with the proposition that good plans must be ecologically sound. This agreement has traditionally had a ritualistic quality, however, in that, with rare exceptions, planners have viewed ecological values mainly as constraints to be addressed late in their analyses, particularly at the behest of environmental regulators rather than at the very core of their mission. And they have rarely viewed ecologists as indispensable participants in their deliberations from the outset.

Richard Forman would change all that, and the argument he lays out in this volume is compelling. Though modern technologies are dazzling, he observes, having enabled us to separate urban residents from their sources of nourishment, potable water, and even jobs, by greater distances than would ever have been imaginable in earlier times, the ''tsunami" of urban growth now threatens widespread disaster. With three billion people living in urban areas, and two billion more expected within the next quarter-century, with global warming, with energy demand rising more rapidly than energy production (the latter, moreover, often with devastating environmental effects), and with the continuing depletion of fresh water supplies and biodiversity we seem to be racing beyond the capacities of our technological ingenuity to shield us from the natural limits of our environment. It is past time, in short, for urban planners and policy makers to recognize ecological health as the single most urgent value to be served by urban planning without which all the others are likely to prove illusory before too many more decades pass.

THE BASIC ELEMENTS OF ECOLOGICAL CITY CONSTRUCTION

Development of a city by the industrial engineering, agricultural engineering, forestry engineering, water conservancy, energy, engineering, tourism, landscape engineering, cultural engineering, environmental engineering, home construction and development capacity building project together. For the eco-city construction is concerned, it also works by some of the above constitutes an organic whole. But, in each specific projects, are required to reflect the eco-efficiency requirements, such as industrial engineering according to ecological principles, the use of circular economic theory, according to meet the design requirements of sustainable development; and energy projects, they are required according to the ecological economics, to establish clean energy projects, through the development of alternative energy and new energy to reduce energy consumption of the ecological damage to the environment; development capacity will have to reflect the sustainable development project, highlighting the development of capacity for sustainable development in the important position.

Ecological function zoning of urban economy

In general, the ecological city zoning in accordance with economic function, can be divided into the following areas:

(1) Human ecological zone, the region is mainly used to reflect the city's cultural connotation. Any city should have its own human-ecological zones, attention to the protection of historical and cultural heritage, through a variety of means to achieve a rich urban culture, the promotion of natural, historical and cultural landscape integration and sustainable use;

(2) Ecological Agriculture Development Area, the development of ecological agriculture in general are concentrated in the suburban area district, which is the human ecological regions outside the city part of the establishment of ecological agriculture development area on the one hand to ease the pressure on the urban environment, and promote the city's environmental balance and eliminate part of the urban pollution, on the other hand the development of ecological agriculture through urban areas to bring economic growth, ecological agriculture;

(3) Ecological and economic coordination and development zones, ecological and economic coordination and development of regional economic development and cultural prosperity are second only to urban human-ecological zones in this area green coverage in general the larger, relatively well developed industry and agriculture, all types of resources needed for economic development or economic factors of development in this region are relatively more concentrated. In this area, for ecological protection and development of both ecological and economic, not only the quality conditions of use of existing ecological and environmental protection-oriented, but also make good use of the radiation from the city center, promotion of eco-economic development;

(4) Cultivating ecological protection zone, which typically are environmentally sensitive areas in the city, is generally not high level of economic development, industrial structure is generally more traditional levels, coupled with low level of industrial concentration, infrastructure is relatively backward, and this part of the region does not advocate large-scale economic development, but rather as the cultivation area of ecological environment and improve the ecological capacity of the city as a whole.

URBAN ECOLOGICAL PROBLEMS ARISING FROM

Urbanization environmental problems caused by lack of awareness

The development of urbanization in Serbia is a key feature of the late start, the starting point is low. This allows us to focus only on the previous economic construction productivity improvement, one-sided emphasis on yield and production value, while ignoring the environmental protection of urban planning and infrastructure construction. City dirty, chaotic, traffic jams prominent. Although with the economy, to our own quality of life are increasingly high requirements, the process of urbanization has gradually accelerated, ecological and environmental problems are also gaining increasing attention, but now for the protection of the environment, and efforts to control capital inputs are not enough, you cannot fundamentally solve the problem of urban ecological environment.

Urban expansion pressure on the environment

With the large number of rural population into cities, cities are unable to meet the functional needs of expanding population, rapid urbanization, industrial and agricultural development in the daily discharge of waste such as wastewater, waste gas, waste, noise and other cities far beyond the self-purification capacity of the environment can bear. Urban functions, changes in the structure of the flow also makes the city the growing population, and changes in consumer attitudes as people, people of the total demand for resources and products is also rising, but the already tense environment to bring greater pressure. Especially in the economic development of the situation also appears under the motor vehicle caused by a series of serious environmental consequences. In addition, the unlimited expansion of the city, or the serious waste of land resources and reduce the utilization of the land, so that greatly reduced the area of arable land, desertification has become increasingly prominent.

As the population increases, the natural population demand for food have continued to increase, to meet this need, the blind expansion of areas planted numerous phenomena, which greatly exceeded the affordability of land resources available, but also by the natural environment to destruction. Second, the population into the cities, housing is the most important issue must be addressed. Housing area increased, not only will develop a lot of land, increasing the burden on the land, while the development of the city to adapt to the changing needs, it must be increased in schools, hospitals and other public facilities investment. Population growth, the supply to the city in the material, social security, employment and energy consumption, transport, emissions and so bring a range of problems. In addition to the human itself, many people exhale carbon dioxide is also increased, to speed up the process of global warming.

SUSTAINABLE DEVELOPMENT AND THE RELATIONSHIP BETWEEN ECOLOGICAL CITY CONSTRUCTION

Resources, sustainable development and the relationship between ecological city construction Resources, eco-city construction of sustainable development is a very important element. The heart of the city as a region, but also the consumption of resources on site. In a city, not enough resources to support the supply of its consumption, in today's society, any resource consumption of a city far more than needed from the city's area to provide. This is the city's sustainable development, it is a very serious problem. Therefore, to set up eco-city, you need according to the requirements of sustainable development, re-planning and building the city's industrial structure, system, and to moderate the reduction of primary industry and the proportion of secondary industry, while promoting increased the proportion of tertiary industry. At the same time, but also continue to promote resource-saving and environment-friendly industries, and reduce resource consumption, reduce unit GDP resource consumption. The construction of ecological city in the meaning of questions is to promote sustainable economic development, and sustainable economic development capacity is also an important consideration in eco-city index. In the eco-city construction, to develop ecological agriculture, industry and services, to pursue economic development and economic benefits at the same time pay more attention to eco-efficiency, ecological benefits to economic development as an important objective. This is the economic requirements of sustainable development, and only pay attention to the ecological benefits of economic development in order to continuously improve the city's ecological carrying capacity, can ensure the sustainable economic development. Therefore, the construction of ecological city, to establish the concept of green GDP, the theory of circular economy should guide economic development, and actively explore the ecological and economic development of the new channel and new way.

Cities are to a certain degree of social development product, eco-city is a necessary requirement for sustainable development of society. In the past few thousand years time, the development of human society is based on the cost of sacrificing the environment, including cities as the core of human society, more serious damage to the environment. However, this is not a social development approach to long term sustainability, with the capacity of the environment more and more weak, the development of this predatory nearly come to an end. Trend can be effective if you do not change, then not only the survival and development of our future generations will be a serious threat to our survival and development of modern people are difficult to maintain. Eco-city construction, is to change this evil, the construction of ecological city not only to protect our survival and development of contemporary human rights, but also to ensure the future survival and development of human rights, that is to promote sustainable social development. In turn, sustainable development of society is to ensure that the construction of ecological city, and only community to sustainable development and harmonious development of eco-city to reach the goal.

CONCLUSION

The city has prospects to become green and healthy city, but to achieve this it is necessary to implement measures of urban ecology. In this role not only to the relevant departments and the level local government, but also the citizens themselves. Although people begin to develop awareness of environmental issues, sustainable development and the importance of preserving the environment, this awareness is necessary to raise to a higher level.

Citizens should participate more in development planning and arranging your own city, or as individuals or organized in local committees and associations. The city is a "living organism" in which it is necessary to create an urban space pleasant to live. Quality space for life, because of its comprehensiveness and orderliness, and even visible communion, is attractive for tourists.

Between human development and nature is a contradiction between a pair of very special in the past few thousand years, human survival and development are predatory. This trend intensified in the last hundred years, resulting in fewer and fewer of our mountains, and various forms of pollution are becoming more serious. However, the contradiction between man and nature are not irreconcilable, and human beings as a natural son, not only to realize that our current approach to development problems, better able to solve these problems. The construction of ecological city is a path to solve this problem, through the construction of ecological city, the development of the city implement the concept of sustainable development, to promote the ecological environment construction and repair, making the city's development in the pursuit of economic and social benefits can also pay more attention to eco efficiency, to achieve social, economic and environmental sustainability, coordinated development, the true harmony between man and nature never were.

REFERENCES

1. Adormbent, M. (1998) *Promoting Sustainable Urban Environments by Continuing Education for Local Authorities*, Urban Ecology, Springer-Verlag.
2. Davies, Z. G. (2011) „Mapping an urban ecosystem service:quantifying above-ground carbon storage at a city-wide scale“, *Journal of Applied Ecology,* 48, p.1125-1134
3. Dramstad,W., Olson, J., and Forman, R., (1996). *Landscape ecology principles in landscape architecture and Land/use planning,* Harvard University, Island Press.
4. Morsan, B., Vahčić Lušić, M., Mladina, I. (2007) „Urbana ekologija i društveni uzroci devastiranja okoliša građenjem“, *Društvena istraživanja,* 3 (89), p. 455-476
5. Peračković, K. (2013) *Osnovni pojmovi u sociologiji potrošnje*, Potrošačka kultura I konzumeruzam, Ivo Pilar, Zagreb.
6. Pugh, C. (2000) *Introduction, Sustainable Cities in Developing Countries,* Earthscan Publications Ltd., London.
7. Stošić Mihajlović, Lj., (2017) *Obnovljivi izvori energije*, VŠPSS, Vranje.
8. Tao, L., Grimm, N.B. (2015) „Comparative study of urban ecology development in the U.S. and China: Opportunity and Challenge“, *Urban Ecosystems,* 18 (2), p. 599-611
9. Forman, R., (2008). *Urban regions, Ecology and Planning Beyon the City,* Harvard University, Cambridge University Press,
10. Črnjar, M., Črnjar, K. (2009) *Menadžment održivoga razvoja,* Fakultet za menadžment u turizmu i ugostiteljstvu, Rijeka.
11. Šimunović, I. (2007) *Urbana ekonomika – petnaest tema o gradu*, Školska knjiga, Zagreb.
12. http://www.sustainabledevelopment.un.org

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GREEN MARKETING IN FUNCTION OF ECOTOURISM AND SUSTAINABLE DEVELOPMENT

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ABSTRACT

Today in the world there is a great interest of the countries to develop tourism sector, in order to utilize tourism as a factor of faster economic development. A new outlook on tourism gives primacy to the environmental dimension of tourism and the implementation of a new concept in development of tourism, which is known as the concept of sustainable tourism development and the development of modern tourism. This concept reflected on a positive relationship between economics and ecological principles. Only tourism can provide continuous maintenance of balance in the natural environment without the risk of impairing the visitors or shift the original character and appearance of the area. Serbia has significant potentials of water resources which can contribute to economic and tourism development in country, but it is necessary to raise public awareness about the need to protect water resources and its continuous monitoring. Green, ecological marketing strengthens awareness and affect other to behave responsibly. The aim of this paper is to show that man's relationship to nature, and especially the water resources must be changed and based on that we conclude that sustainability is a fundamental principle of any business, including ecotourism.

Key words: ecotourism, sustainable development, green marketing, new trends in tourism development.

INTRODUCTION

Rapid development of ecotourism in world means a new behavior of participants in tourism movements through spiritual enrichment of personality, with a meaningful relationship on natural and anthropogenic tourist values. Ecotourism is rapidly evolving in line with modern trends and offers to tourists around the world various forms of ecological tourism products. The adoption of the concept of sustainable development and management of ecotourism, using the experience of other countries, can contribute to the proper positioning of Serbia as ecotourism destinations on the international tourism market.

Development of ecotourism in Serbia is still in its infancy. The main reason for that is lack of motivation, primarily because of low profitability. As exceptions to this rule should be several protected areas like: Zasavica, Carska Bara i Palić-Ludaš. It is particularly important that development of ecotourism in Serbia be directed on repositioning of Serbia as a tourist destination in international market by creating a desirable image of the country with a wealth of natural resources.

The role and importance of water resources is huge because people, animals and plants cannot survive without water. Water runs, initiates, but also limits the development of any economy, society, family, or the whole human race. Water is the foundation of life, the articulation of survival. Water is not a commercial product like other products, water is the heritage that must be protected, defended and treated as such. [1] Sustainable development reflected on development that meets the needs of the present generation in order to provide the same needs for future generations. We can emphasize that focus of sustainable development is more on economic development, social development and environmental protection for future generations. [2]

THE CONCEPT OF SUSTAINABLE DEVELOPMENT OF ECOTOURISM

As the world's economic sector, tourism achieved a leading position compared to other industries in the end of the 20th century. As fastest growing industry in the world, tourism is extremely difficult to control. It takes a significant responsibility in relation to the economic, social, cultural and natural environment. For this reason, in front of tourism industry and all institutions in this field sets a task for establishing, first of all, a sustainable and responsible development in order to preserve all the important values of the environment, as part of the tourism product, and achieve essential balance in which meet current needs of tourists will not compromise meeting the needs of future generations. In the last two decades, tourism has developed into an important factor in the context of sustainable development. In the professional literature there are synonyms for the same thing, such as, responsible tourism, eco-tourism, natural tourism and ethical tourism. Ecotourism is responsible tourism, which is friendly related to natural and cultural heritage [8].

Ecotourism performs a minimal impact on the environment and local culture, while helping gaining profits, jobs and protection of local ecosystems. Ecotourism means "any type of tourism, which contributes to the environment protection, social and economic improvement of integrity and natural, generated and cultural values on a continuous basis" [8]. The main objective of this type of tourism is to enable people to enjoy and learn about the natural, historical and cultural characteristics of unique environments, while preserving the integrity of the city and promote economic development and welfare of the local community. Ecotourism is based on a number of development principles: [7] It is based on nature and depends on the natural environment, which does not exclude forms of cultural space; It is environmentally sustainable and use the environment in a way that does not disrupt the harmony of nature, which is in the interest of the tourism; it is environmentally instructive. Requires the presentation of the rules of conduct that encourages visitors to behave in such a way that creates a less negative impact on the natural and socio-cultural environment; It is locally useful.

It is necessary that local communities understand the importance of eco-tourism and actively be involved in its development, in order to achieve the benefits for themselves and for the natural environment in which it develops; It is an experience for tourists to stay in touch with something that is natural, original, ancient and undisturbed by modern lifestyles. The development of eco-tourism includes an integrated approach to its planning and management. This can be achieved through a combination of the needs of traditional urban management (transport, land exploitation planning, marketing, economic development, fire protection) and the needs of planning tourist activities. The purpose of sustainable development is to enable the development of ecotourism in a way that tourists see and experience what they want, but without destroying same factors that attract them. On the other hand, society, culture and environment of the people who live in tourist destinations are not destroyed nor threatened, so it is the task of the tourism industry to communicate with local communities and to involve them in development.

Considering that humanity increasingly faced with many inequalities within and between nations, with the increase hunger, poverty, disease, etc., a major threat to the future are the environmental consequences like ozone layer reduction, climate changes, land degradation, air and water pollution. Therefore tourism, with its position in the world economy, has a moral responsibility and interest to take the lead in achieving the transition to sustainable development. In the framework of EU, tourism is one of the largest economic sector with 9% of employees and 9% of the consumption. It also represents one of the five export categories in 83% of all countries in the world and a major source of foreign exchange earnings in almost 38% of the countries. Thus has a major role in the economy of many countries, as a source of employment and a way of fighting poverty. According to forecasts by the World Tourism Organization (WTO), the number of tourist arrivals in Europe will be doubled by 2020, amounting to 720 million. This expected development has serious risks for the environment and the population welfare, but also for tourism as an economic sector [10]. Also, it is noted that most of the tourists avoid destinations with impaired environment. The journey becomes faster, easier, while the most distant destinations are relatively accessible. Finally, tourism in EU countries is one of the most important social and economic activities, which employs over seven million people [10].

GREEN MARKETING, ECOTOURISM AND WATER RESOURCES

Environmental threats that shook Serbia in recent years and decades in some way, influenced on development of new marketing activities – in the form of green marketing. Some number of consumers (citizens and organizations as well as consumers) become aware of the true danger and ready to take certain steps. Green marketing has evolved in the direction of creating marketing activities respecting the natural atmosphere. The importance of green marketing is nowadays imposing. Almost all companies operating in Serbia must be responsible and protective in relating to the environment and water resources. Overall, green marketing activities relating to: rational use of non-renewable natural resources, reducing waste through recycling, preventive actions to protect and improve the environment and others.

The role of green marketing (IMC- Integrated Marketing Communication, in particular) is extremely important in order to be proclaimed social responsibility to a higher level. Public Relations as a relevant element of IMC in green marketing is needed to start the citizens to do useful things for their city, nearby rivers, forests ... to actively participate in environmental actions and to promote volunteer work, to raise collective awareness and the importance of social responsibility. Key activities in order to be implement in the near future through marketing communications can be: Raise awareness of the general public in Serbia about the importance of nature, the environment, particularly on water protection; Practical application of the EU rules, especially in the area of water resources; Continuous monitoring of water quality, both in the rivers and lakes of Serbia, as well as outside the borders; Further development of legislative norms; Further cooperation in bilateral and multilateral relations; Extensive education of the people; Institutional development and others.

Environmental changes, influence of the media, market trends, etc., conducted a noticeable impact on consumer behavior as well as to new approaches and activities in marketing. Marketing activities provide that people more respect the natural environment - how to water, and other resources. The role of electronic, print and other media in the range of protection of water resources, taking concrete steps is undoubtedly valuable. Promoting green concept of marketing educates citizens and matures their awareness. River pollution is a prominent problem of our time, and together can significantly reduce the pressure on the further deterioration of water quality. In any case, the "green" market segment is increasing. Green consumers are at the forefront of a strong value system, to actively participate in environmental protection activities, seeking information about green products and want transparent communication with the companies. [3, str. 63] Green has become the symbolic word for something that is purely on environmental issues. Many companies are trying to emphasize "green" activities to acquire such an image, or to sell "green" products with a higher price. Presentation of the "green" image of the company is desirable if it is sincere.

Authorities in Serbia carried out some promotional activities in function of raise awareness about the use of water resources. But, it cannot be concluded that achieves the desired positive result. The problems are reflected in the uncontrolled deforestation and neglect the existence of waste, which reduces the quality of water resources. The solution exists in enhanced care and protection of river sources, planned afforestation, small dams, recycling system, the construction of modern landfills and others.

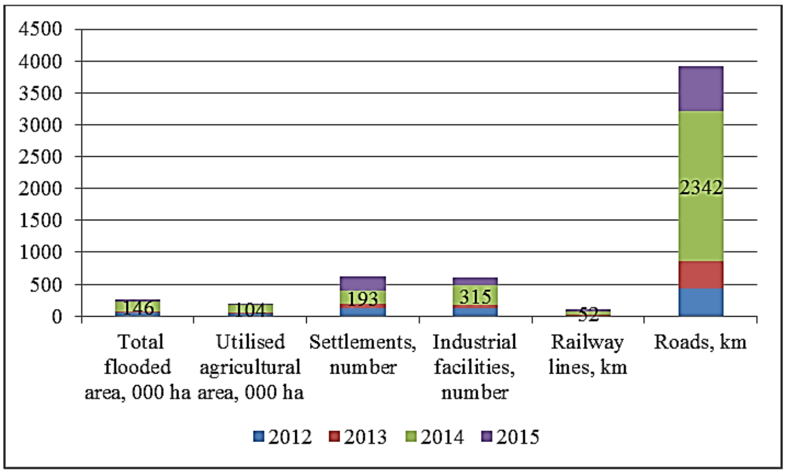

Figure 1. Flooder areas in Serbia

In Figure 2 can be seen total consequences of natural disasters in recent years in the Republic of Serbia. Since 2009, Serbia is in a constant struggle with natural disasters. In 2009, Serbia was hit by two adverse natural events: floods and extreme winter temperatures, which were not on large level, but it represent a great reminder of nature. In 2013 began pouring rivers and in 2014 it spills into a real disaster with the greatest economic and human consequences in the period. This disaster, followed by the outpouring of rivers and floods claimed the lives and caused extensive damage and the consequences of economic development.

In the coming period are expected intense and alternating disastrous events. [12, p. 4] This will be reflected in the relevant water areas of the Republic of Serbia. A few years ago, in May 2014, floods are extremely bad influence on almost 2/3 of the country, destroyed more than 400 and damaged more than 30,000 homes. The total economic damage has exceeded 1.7 billion. This event confirmed that damage from floods and droughts depends on the exposure of the population, economy and society and their capacity to adapt.

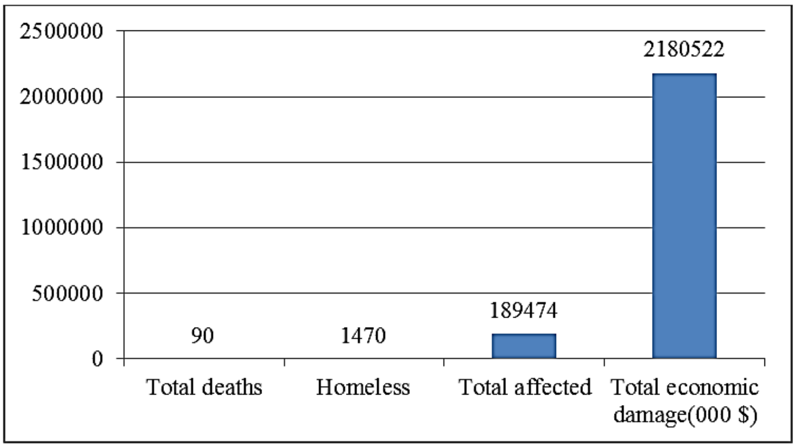

Figure 2. The consequences of natural disasters on the economy of the Republic of Serbia from 2008 to 2015 [17]

The need for water is likely to rise as a result of climate change. [13] In any case, without a strong, energetic and broad public support, it is impossible to count on the improving problems in the use and protection of water resources. This implies a high awareness of the citizens in terms of ecology and high culture of responsible behavior - both adults and the elderly, as children as a youth.

ASPECTS OF ECOTOURISM IN SERBIA

Tourism contributes to the development of culture, traditions and beliefs of people. To call some place tourist place it should, as a product, satisfy preferences of people. In order to satisfy the needs of tourist some destination must possess a natural, wealth, tradition, culture, and global tourism offer. To a certain destination has to offer tourists, must be sustainable tourist region, and must constantly work on improving and developing destination. [18]

Ecotourism in the world is quickly becoming the most popular type of holiday. According to the World Tourism Organization, tourism recorded an annual increase of 5% on a world scale, which represents 6% of world GDP and 11.4% of consumption. [8] Like all forms of sustainable tourism, eco-tourism is a dynamic area, with new techniques and approaches being developed every year. It is a small but rapidly growing industry within which operates mainly small and medium enterprises.

Ecotourism is a subcomponent within the field of sustainable tourism and sets as an equivalent nature-based tourism. Basic components of eco-tourism can be systematized as follows [9]: contributes to the preservation of biodiversity; maintain the well-being of the local population; includes experience of interpreting and learning; includes responsible action on the tourists and the tourism industry; directed primarily to small groups by small businesses; requires the lowest possible consumption of non-renewable resources; emphasizes local participation; ownership and entrepreneurial opportunities especially for the rural population.

It is particularly important to the development of ecotourism in Serbia should be not only a means to achieve an overall sustainable development of tourism, but also an adequate approach to the repositioning of Serbia as a tourist destination in the international market, creating a desirable image of the country with a wealth of natural and cultural resources. According to the World Tourism Organization, ecotourism global share in total tourist trips between 2 and 4% [11]. Bearing in mind the trends in our country and the developments in the domestic tourism market, it can be estimated that the share of Serbia even lower.

However, the launch of ecotourism is quite demanding, because such arrangements require full commitment to society, and there are many limitations: the lack of minimum infrastructure; low level of environmental awareness; Desire for improved living standards; the absence of clear standards and legislation. However, its diversity of potential, Serbia can fully meet modern requirements of active tourism and can be presented in accordance with sustainable development and preservation of environmentally protected areas.

CONCLUSION

As a powerful instrument of development, ecotourism can actively participate in the sustainable development strategy. The active contribution of ecotourism presupposes solidarity, mutual respect and participation of all actors (both public and private) involved in this process, and must be based on efficient cooperation mechanisms at all levels: local, national, regional and international. To participate in sustainable development, eco-tourism must be based on the opportunities offered by the local economy. He should be fully integrated into and contribute positively to local economic development.

The development of tourism based on sustainability criteria, should be long-term environmentally acceptable, and economically vital and ethically and socially equitable for local communities. Sustainable development is a guided process which envisages global management of all resources, especially water, so as to ensure their vitality, enabling it to be preserved our natural and cultural wealth, including protected areas. Serbia has ideal conditions for the development of eco-tourism but ecotourism is now at an extremely low level of development.

Way of using precious water resources would have to be changed and green marketing is another name for accountability in this area. Water resources in Serbia have significant problems, and the problems are primarily related to the management of this resource, especially as an essential source of water development and eco-tourism on a sustainable basis. The key concept that should include a new approach refers to the flexibility of the system to respond quickly to natural disasters, and management of natural disasters must become part of an independent planning of economic development, not just part of the continuing humanitarian aid.

REFERENCES

1. Directive of the European Parliament and of the Council 2000/60/EC Establishing a Framework for Community Action in the Field of Water Policy).
2. Štrbac, N., Vuković, M. Voza, D., Sokić, M., (2012), Održivi razvoj i zaštita životne sredine", Recycling and Sustainable Development, Vol. 5, No. 1, pp. 18-29.
3. Milovanov., O. (2015), Marketing and Sustainability: Identifying the Profile of Green Consumers, Strategic Management, Vol. 20, No 4., University of Novi Sad, Faculty of Economics in Subotica.
4. B. Rabotić., B., (2013), Selektivni oblici turizma, Visoka turistička škola strukovnih studija u Beogradu.
5. Stanković, S. (2008), Turistička geografija, Zavod za udžbenike Beograd.
6. Jovičić, D., (2011), Menadžment turističkih destinacija, Geografski fakultet Univerzitet u Beogradu,
7. Smith, M., Macleod, N., Hart Robertson, M., (2010), Key Concepts in Tourist Studies, Sage, London, 2010.
8. E. M. Wood, (2002), Ekoturizam - principi, postupci i politike za održivost, Centar za odgovorni i održivi razvoj turizma, Beograd.
9. Nikolić, S., (2006), Turizam u zaštićenim prirodnim dobrima Srbije, Zavod za zaštitu prirode Srbije, Beograd.
10. D. Fennell, R. Dowling, (2003), Ecoturism policy and planning, Department of Recreation and Leisure Studies, Brock University, St Catherines, Ontario, Canada.
11. Harris, M. J, (2009), *Ekonomija životne sredine i prirodnih resursa: Savremeni pristup*, drugo izdanje, Datastatus, Beograd.
12. Panel ekspertske grupe o klimatskim promenama – IPCC – 2014. http://www.ipcc.ch/report/ar5/syr

13. Publikacija: "Vode Srbije – U vremenu prilagođavanja na klimatske promene", Ministarstvo poljoprivrede i zaštite životne sredine R. Srbije - Agencija za zaštitu životne sredine, Beograd, 2015,
14. Durkalić., D., Kostić., M. i Riznić, D. (2015), Održivo korišćenje prirodnih resursa kao nosilaca zelene ekonomije, *Ecologica*, No. 79, pp. 528-532.
15. EBRD, Transition Report 2015-2016
16. International Monetary Fund, World Economic Outlook Database, 2015
17. EM-DAT International Disaster Database – Centre for Research on the Epidemiology of Disasters, http://www.emdat.be/advanced_search/index.html
18. Durkalić., D. (2015), Vrnjacka Banja as a tourist brand or tourist region, Challenges of Contemporary Economies in the Face of Global Market Conditions, Cracow University of Economics, Cracow, Poland, pp.229-239

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ECOLOGY AND FUNCTIONALITY OF GREEN AREAS OF THE VILLAGE RAJAC

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ABSTRACT

This area that represents the wine producing core in Serbia isn't used today according to its significants and potential despite sistematic work on protection and revitalization. Researched region doesn't represent a part of wine system today as it should be based on its significants, position and value – not by use and not either by funcional coherence. During the analisis of the current state in the area of village Rajac, different problems were detected which influence on the decrease of ecology and funcionality of green areas. Based on that research here are given the appropriate suggestions for their reconstruction and advancement.

Key words: ecology, funcionality, green area, Rajac.

INTRODUCTION

Greenery has a critical role in determination of the level of certain landscapes or at least in evaluation of one landscape benefits for a longterm stay. Green spaces in urban areas represent a specific living „constructional material“ within physical structure of the place. They change their shape and polichromy depending on the seasson, so therefor changes the apperance of the rest of the elements of physical structure of the place in whose forming they participate.[1] Green spaces appear like an independent element within physical structure of the urban area aswell, with clearly defined functions. They not only represent the most flexible element of the areas physical structure, they are also significant based on their „phisical apperance“ for overall spatial introduction of a certain place and its ambiental, sociological and ecological value. Green spaces are directly used for active and passive recreation of population, while indirectly influence the raising of environmental quality with their existance.[2] In order to be avaliable for the population, grean spaces should be well incorporated, good quality and equaly distibuted in areas tissue apropos conected into unique system of greenery. Plants of green spaces represent irreplaceble nature elements with their shape, form and life funcions which contribute to melioration of environment at its widest sence.

Rajac represents the core of wine producing in Serbia is not used today according to its significants and potential despite sistematic work on protection and revitalization. This wine region does not represent a part of wine system today as it should be based on its significants, position and value – not by use and not either by funcional coherence. Rajac is located in Eastern Serbia, in the valey of the lower course of the river Timok, in so called, lower zone of Negotin Krajina on a railway track Negotin – Zaječar, 22km south from Negotin. Settlement belongs to municipality of Negotin and it is located on 44° and 15' North latitude i 22° i 15' East longitude and covers an area of 12.9 km2 .[3]

WORKING METHOD

Working method was based on multidisciplinary activities which included many other disciplines such as: pedology, geography, forestry, architecture, construction, geodesy, meteorology, hidrology, etc... and all in order of creating an optimal living environment and relaxing of residents, taking care of health, technical, functional and economical needs. A part of activities included creating of as effective and as functional conditions as possible for certain area. In order to gain a complete image about existing green spaces in researched area, conditions of the area were examined in details, and later on were given sugestions of possible development.

RESULTS AND DISCUSSION

In order to speak about ecology and funcionality of this area and how to rise it a level up, at first it was determined a character of the landscape itself with an accent on vegetation and green areas. It has been established that the area of Rajac includes two types of landscape characters „Underhill and hill ground of vineyards" and „Alluvial plain with river valley forests and arable lands".[4] If we look back on already mentioned detailed researches of landscape character and its ecology and funcionality it is noticeable that a great potential has a few funcions of green areas in Rajac. However all of these funcions are on a very low level and evidently needs improvement.

Biological - sanitary - hygienic function

Green spaces in rural areas which are mostly consisted of indigenous species have a unique biotechnical atributes, such as: significant durability, sustainability, eficiant functioningeven in difficult environment conditions, easier and more simple maintaining, quicker revitalisation.[5] Rural areas do not have a significant fond of allochthonous species. Overly introducing and propagation of certain species and its excessive number whish has usually been realized on account of the spread of some other species is a common cause of structural imbalance of dendroflora and monotony of landscape which is the case in Rajac although Rajac is rich in greenery and numerous variety of species. Forest that is located between the village itself and wine cellar has a great role when it comes to this funcion, however it is insufficiently used and its funcionality is at its minimum. Considering the fact that in this area where usually grow oak and beech forests it is noticeable growth of acacia which is considered an invasive species, as well as sour tree (Ailanthus altissima), in order to improve biological funcion it is suggested their eradication and their exchange with plants of beech as an indigenous species. Since the forest is located at a very steep ground it should be devided into three zones. On the highest peack an oak would be kept (Quercus cerris, Quercus frainetto), which would confluence into beech as the ground goes lower (Fagus silvatica), whereas in the lowest zone we suggest planting of purple (Prunus cerasifera atropurpurea).(Image 1A) This type of solution would significantly contribute on the visual effect of the forest itself considering that choosen indigenous species own an interesting change of color during different seassons. Also this type of solution would contribute to engineering function and stopping soil erosion in the abundant precipitation.

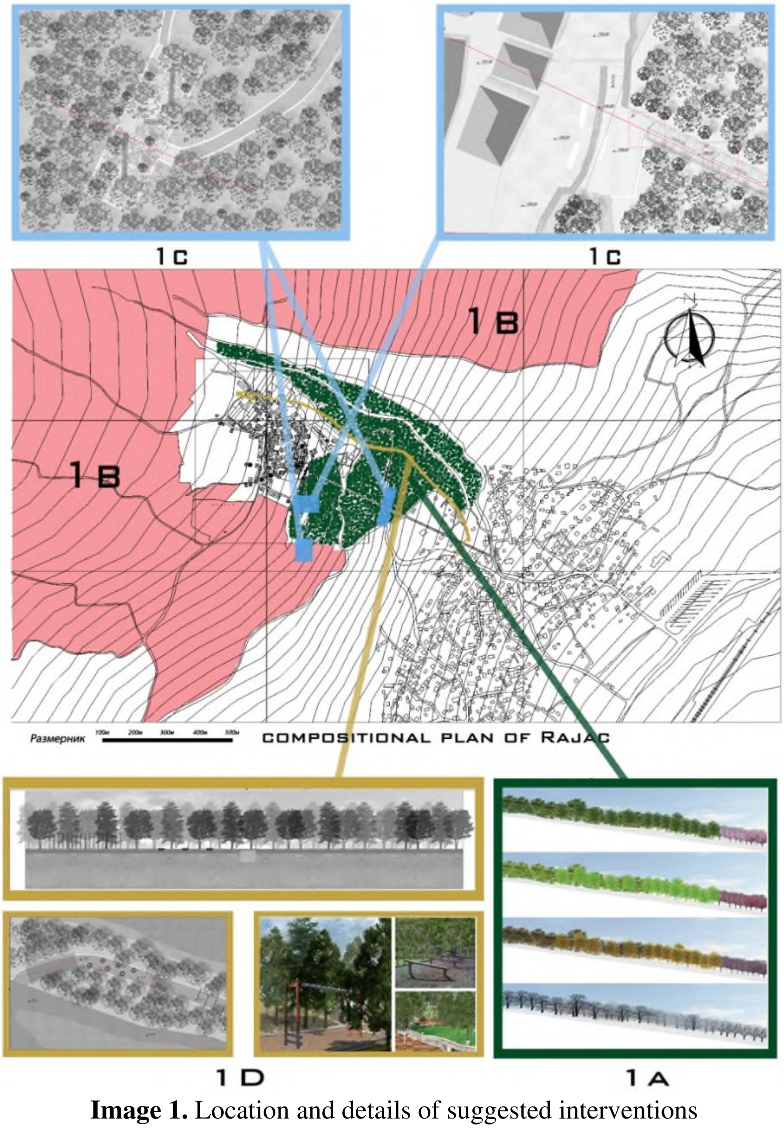

Image 1. Location and details of suggested interventions

Decorative – estetical function

It is especially important because it defines structure and integration of settlements and surrounding space in one unit which contributes identity and diversity of settlements. Green spaces in Rajac are part of estetic, historic and cultural heritage which gives a natural balance to built environment. Modern planning demands creating of harmony when creating an unique unit between architectural and biological elements during which it must be payed attention about usage and function of area. With previous suggestion this function was partialy included, however Rajac owns on its own a greater potential to improve this function. Longterm measures of development include regeneration which before everything else means reconstruction of grape growing.(Image 1B) Therefore it is suggested an incitement of conversion of neglected land into vineyards, including the revitalization of old vineyards and their protection. On this location has been noticed an extreme presence of invasive species Ailanthus altissima, therefore it is suggested its eradication and removing young plants which appear spontaneously. Suggestion is to plant decorative indigenous species: Tress (Juglans regia, Quercus cerris, Quercus frainetto, Morus alba, Tilia sp., Fraxinus ornus, Carpinus betulus...), Fruits: (Pyrus sp, Malus domestica, Prunus domestica, Prunus persica, Prunus avium, Rubus idaeus...), Shrubs (Ligustrum vulgare, Syringa vulgaris, Buxus sempervirens, Rosmarinus officinalis, Prunus laurocerasus, Cotoneaster sp., Pyracantha coccinea, Viburnum lantana...), climbers (Vitis vinifera, Hedera helix, Lonicera caprifolium, Parthenocissus tricuspidata...), perene (Rosa canina, Iris sp., Salvia officinalis, Ruscus sp., Calendula arvensis, Vinca maior, Hosta sp.,Thymus sp., Primula sp...).[6] Considering the fact that we are talking abour rural spaces it is especially important for this space to be not just „nice“ but it should also be settled based on ecological values. Ecological value of vegetational elements in public areas is refered on choice of species which relate carefully and with balance to environment while participating with it. It takes into account the laws and demands of natural environment in which it lives, never compromising it and including itself into its ways.

Culturaly – educational function

This function refers above all on introducing citizents to the world of plants in general and especially with species that live in this area. Green spaces play a significant role in development of social life of its users. Not only that a posibility of meeting and introduction show a direct positive influence on its users, but visual perception of open area gives a sensation of free moving that represents important factor for human mental health. Green spaces are sources of education, making spaces suitable for structural and unformal longterm learning about nature, ecological process and environment process. If we consider a rich history and cultural heritage of Rajac it gives a wide spectar of possibilities for this functions growth. Bounding plants itself, especially in the area of wine yards, for events from closer and further history contributes to development of bonds between spiritual and historic values of people that lives there and who visits this place and influences positively on capability for longterm from instantaneous benefits, big from small values. Considering that Rajac is rich with vegetation it is possible to form platforms which can contain big ilustrated and decorative tables in representative places which will inform visitors about the basic funcioning of plants. They would provideintroducing with vegetation that grows in this area and in that way to bring closer the efficiency of every single tree and would be motivation to those who are responsible for taking care of greenery. Those could take place in a forest mentioned above through which visitors pass on their way to wine yards.(Image 1C) Also, this kind of areas emphasis an identity of neighborhood and often become estetic or simbolic referent point, making streets and neighborhood more living. Pleassure and way of usage of areas during meetings represents an important social aspect of every area. Sociological value of public areas is closely related to spending time off when citizens are free from work but not from social activities in their community together with other customers that spend time based on their own choice and affinity. Meeting and get-togethering of people can provide even very small areas in the village with active content which represent real „oasis" for recreation and relaxation.

Recreational function

Green areas provide space for recreation (active and passive), playing sports, or for children to play. For the health of the human body is particularly important that the person engaged in recreational activities in the natural environment and that part of his free time in touch with nature. [7] Many green spaces in Rajac except for the lack of profitability in the direct sense is characterized by a significantly reduced overall functionality (which can be seen as indirect profitability). Here public spaces exist in a state of barely better than complete neglect, and therefore reduced functionality. In the case of the central zones, with a location that is very attractive and residents exposed to view, usually their condition can be described as relatively good. Everything is moving towards the periphery areas are deserted and less functional. According to these problems and potential which Rajac has one of the possible solutions for the improvement of this function is the formation of a recreational park. This park would be located in the forest. It is a combination of green and jogging paths with exercise equipment. This path provides multiple activity for users: physical activity for a wide range of visitors, also non-sport visitors, fitness training, relief as a family experience. Given that this is a rural area would not be used classical instruments of exercises such as those in urban parks, but they would be designed as a physical barrier which the user has to take in order to continue your journey, such as rope, wooden beams, ladders, laid automotive rubber etc. (Image 1D) In addition to physical activity park would offer users opportunities to explore space. During walking or running on the track users have a sense of anticipation, because they know that's next obstacle in the form of green expected. A sense of intrigue that forces the user to continue his journey takes him to the end of the park. After the last obstacle person comes to the entrance into the same wine yard where they can refresh and rest.

Economical function

In recent years, increasingly gaining in importance, especially if one takes into account that built or renovated green areas should be sustainable, although they represent unprofitable areas. Economic value of the green areas is interpreted via the corresponding beneficial effect of greens. Economic benefits should be visible on the site, such as direct employment that planned area, places to play and other green areas allow for the local population, and the possibility for a marketing operation such as wine-growing community or fruit that give income by selling products to residents and visitors. Attractiveness of the Rajac area in terms of tourism can not be abstract, but stems from the attractive attributes of the tourism area - recreational, curiosity , aesthetic and famous. Each of these attributes is working on the possibility of using the area for tourist purposes, or gratification of tourists needs. Certainly, the mentioned attributes have a relative value which is subject to change, depending on the temporal and spatial relations and demand trends in the tourism market. Interdependence relations man - attractiveness, in this type of tourism is not only very high, but it significantly affects the function of the space as a component of the tourist offer. No human activity and the activity is not so much dependent on the characteristics of the area such as tourism and recreation. Cities and areas such as the Rajac, with suitable environmental conditions, high attractive attributes, adequate reorganization of time could grow into a well-attended tourist destination.

CONCLUSION

Based on all of the analysis done, it can be concluded that the study area has provides highly potential for further development and restore the status of the leading wine center in the region. The analytical procedure that was carried out has established some general guidelines that contribute to constructive future activities in the study area. First of all it is necessary to implement the guidelines at a strategic level that form the basis for further development of the entire area, and then the guidelines at regional and local level when it comes to green areas. For the fulfillment of the guidelines relating to certain places (point) in the area, proposals have been offered. For a detailed drafting of such a project in a professional practice is necessary to do more "prototype - projects" and do more accurate valuation. Improving the number and complexity of the criteria for the evaluation of valorization extinguisher must be accurate and give more specific results. Defined guidelines and suggested solutions may constitute the basis for defining the conditions for improvement in any area, the experts and the legislation that pays more attention to improving the environment and functionality of given location. [4]

REFERENCES

1. Anon.,: Valorizacija i tipizacija zelenih površina Sarajeva prema funkciji, znacaju i položaju unutar fizicke strukture grada, 1-3, master rad, Visoka škola strukovnih studija, Čačak, n.d.
2. Anastasijević, N.; Vratuša, V. : Održivost zelenih površina naselja, 8th Symposium on Flora of Southeastern Serbia and Neighbouring Regions, 167-173, Niš, 2005.
3. Žikić, A., Đorđević, Ž.: RAJAC vinogradarsko naselje Donjeg Timoka, Kulturno - prosvetna zajednica Srbije, Beograd, 1999.

4. Đukin, A.: Mogućnosti revitalizacije kulturnog predela sela Rajac, master rad, Šumarski fakultet, Univerzitet u Beogradu, 2015.
5. Ljujić-Mijatović, T.; Mrdović, A. : Proizvodnja cvijeća i ukrasnog bilja, Univerzitetska knjiga, Sarajevo, 1998.
6. Plan detaljne regulacije kompleksa rajačkih pivnica u opštini Negotin – nacrt, Republički zavod za zaštitu spomenika kulture, Beograd, 2015.
7. Mekić, F.: Rasadnici i nasadi, Šumarski fakultet u Sarajevu, Sarajevo, 1998.

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THE TAXONOMIC ANALYSIS OF THE LAWNS OF SPORTS AND RECREATION COMPLEX AT IBAR QUAY IN KRALJEVO

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ABSTRACT

This paper presentsa research whose subject is the taxonomic analysis. Based on researches we got results about numerical condition of families, genera and species of lawns.In lawns that have been researched, there have been found 85 plant taxa. In the flora of analysed lawns it was recorded a presence of 68 genera and 27 families. The most frequent were representatives of a family Gramineae Juss., and among the most frequent generas in the researched area were genera *Rumex* L.And *Poa* L. The conclutions will serve as theoretical frame for further development and improvement of the lawns.

Key words: lawns, quay, green space, family, genera, Kraljevo.

INTRODUCTION

The role of urban green spaces in the human life and development is very important. Studied area is located in the urban fabric and has a great impact on the modification of the microclimate conditions, and therefore the comfort of residents of Kraljevo. Today the development of urban areas is characterized by increasing construction. The representation of objects of landscape architecture is at a low level despite the growing functional and environmental justification related to the improvement of environmental quality. Grasslands are an integral part of Dot's all green areas, and often their only element. Grass surfaces are very suitable for conducting a variety of sports activities, as these are places with fresh, purified air and a pleasant atmosphere for socializing, enjoyment, relaxation, recreation and entertainment. Consistent green lawn area is favorable to the eye and makes the landscape view pleasant for the eye [1]. Recreational areas under lawns except decorative, recreational, psychological, ecological functions have sanitary-hygienic function and represent a part of the municipal system of the city. Analysis of lawn urban spaces in a straightforward way indicates that on the sowed intensive maintained lawns surviving species are those that toleratemaintaining care measures. Also, in urban areas is much easier to grow, develop and survive for the plant species that grow by nature in the region [1]. Analysis of the lawn of the Ibar quay is very important to determine the direction of further development and current state of this open public space, which is of great importance for the city of Kraljevo [2].

MATERIALS AND METHODS

In the analysis of botanical structure we used the method of Braun Blanquet (1964) [3]. Exploration was carried out during 2016. The lawn surfaces which were researched, were determined sothat they uniformlycover all the parts of the quay which are under the lawns. At the field were taken 10 phytocoenologically records from following surfaces of Ibar quay: 1. athletic stadium Ibar quay - grassy area of a football field; 2. Playground, grassy playground surfaces; 3. Ibar quay, grass surface on a slope near the promenade; 4. Walk on the quay, decorative grass flat surface; 5. Ibar quay, parking zones, surface grass on a slope, 6. Ibar quay, grass area along the coast; 7. Ibar quay, a grass surface that is flooding near the stadium; 8. Ibar quay, grass area along the river Ibar near the town beach; 9. Ibarquey, grass area along the bank of the river Ibar near the walking paths; 10. Ibarquey, near the tennis courts, grass surface on slope. Minimum area of phytocoenologically recording of the studied area was 20 m^2 and a maximum of 100 m^2. The total area of phytocoenologically shots is 495 m^2. At the point of taking phytocoenologically footage using a GPS device (iGO primo) was measured elevationand recorded the geographical coordinates. Exposure field was determined by the compass. Cover was estimated by ocular route and is described in percentages. Height of the pitch is determined with the aid of an instrument for measuring the height (British Standard 30: Part 3: 1991) [4]. The plant material was collected, herbarized and determined at the Faculty of Forestry, University of Belgrade. Determination of the plants was carried out by using relevant literature: 'Flora SR Srbije' I-X (1970-1986)[5], Šarić (1978)[6], Lanzara & Pizzetti (1984)[7], Kojić (1986)[8], Mišić & Lakušić (1990)[9], Javorka & Csapody (1991)[10], Ocokoljić & Ninić-Todorović (2003)[11] and Stavretović (2008)[12].

RESULTS AND DISCUSSION

On the field was taken 10 phytocoenological shots of lawns. Investigated lawns of green areas at Ibar quay include 5 types of pitch. These are decorative lawn, lawn slopes, dry grassland areas, floodplains and lawn for sports fields. At the investigated grass areas it was recorded the presence of 85 plant taxa. The flora of analyzed lawns was recorded 68 genera and 27 families[2] (Figure 1). Analysis of the taxonomic characteristics of grass quay area shows that the represented four families with more than three plant taxa, and four families with the three plant taxa, that is a total of 61 (71%) of plant taxa (Table 1).

Table 1. Represented families with 3 or more than 3 species of flora in the lawn of sports - recreational complex on the Ibar Quay

Families	No. of species	Percentage(%)
Gramineae Juss.	17	20
Compositae Giseke	16	19
Leguminosae Juss.	8	9
Polygonaceae Juss.	8	9
Cruciferae Juss.	3	3,5
Rosaceae Juss.	3	3,5
Labiatae Juss.	3	3,5
Plantaginaceae Juss.	3	3,5
Total	61	71

The most common are the representatives of familie Gramineae Juss. It includes 17 species and 20% of the total number of present plants, family Compositae Giseke includes 16 species and 19% of the total number of plants present, followed by the family Leguminosae Juss. 8 which includes the plant species or 9% and Polygonaceae Juss. 8 includes the type of plant or 9% of [2] (Figure 1).

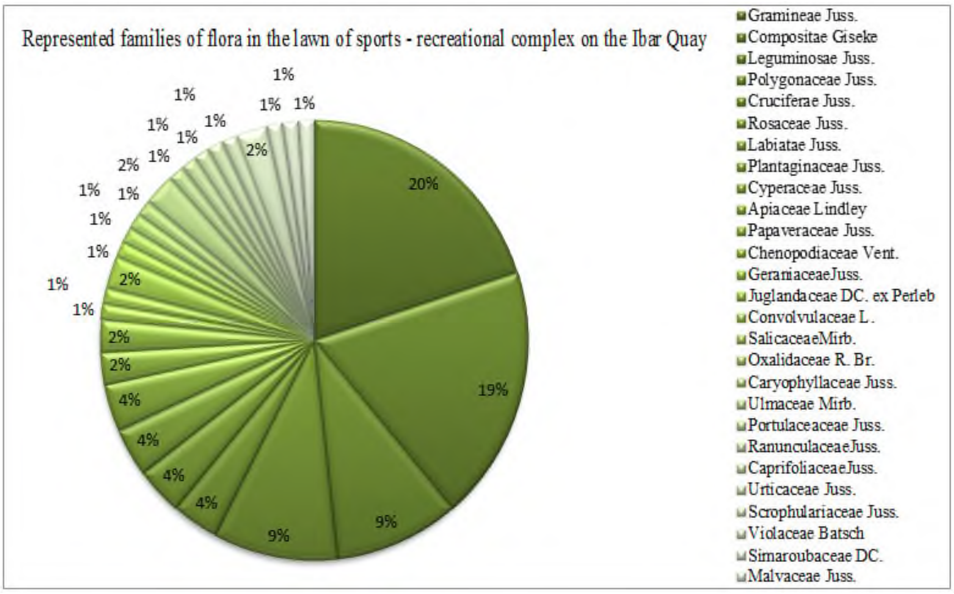


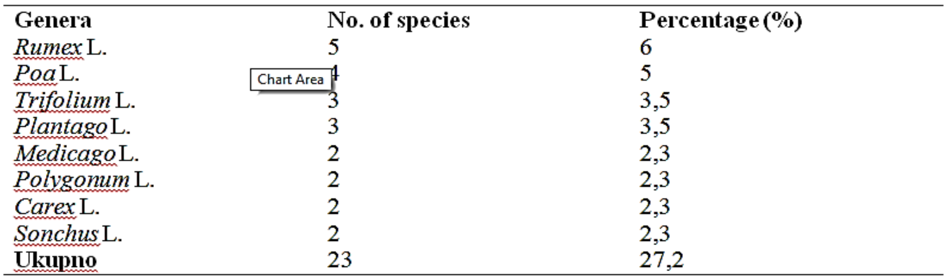
Figure 1. Represented families of flora in the lawn of sports - recreational complex on the Ibar Quay

The presence of species of the family Leguminosae Juss. (9%) indicates the absence of tending and maintenance measures of the lawn because species *Medicago sativa* L., *Trifolium pretense* L., *Vicia cracca* L. of this family are present in the tested area and they are not resistant to cutting and stepping so therefore the conclusion regarding the maintenance [2]. A large number of species in the family Polygonaceae

Juss. is due to ecological characteristics of habitats at quays, dominated nitrophilous habitats and high humidity, which is characteristic for the presence of species of this family. Also, the high share of species indicates a large extent on the anthropogenic impact [13]. Into composition of the flora of analyzed lawn most represented families are those which by the number of species and genera are distinguished by the highest richness in the flora of Serbia [13]. Research flora of the pitch of the quays (Petrovic, 2015) [14] shows almost the identical spectrum of the listed family. Thus, according to the aforementioned research, family Gramineae Juss. is the most frequent, followed by the families Compositae Giseke, Leguminosae Juss., Cruciferae Juss., Labiatae Juss., Apiaceae Lindley, Polygonaceae Juss., Caryophyllaceae Juss., Rosaceae Juss.

Presentplants are classified in 68 genera. Anlysis of taxonomic characteristics on genera level shows that 8 generas are present with more than two plant taxon, in total with 23 (27,2%) of plant taxons (Table 2).

Tabel 2. Presence of genera with more than 2 species of flora in the lawn of sports - recreational complex on the Ibar Quay

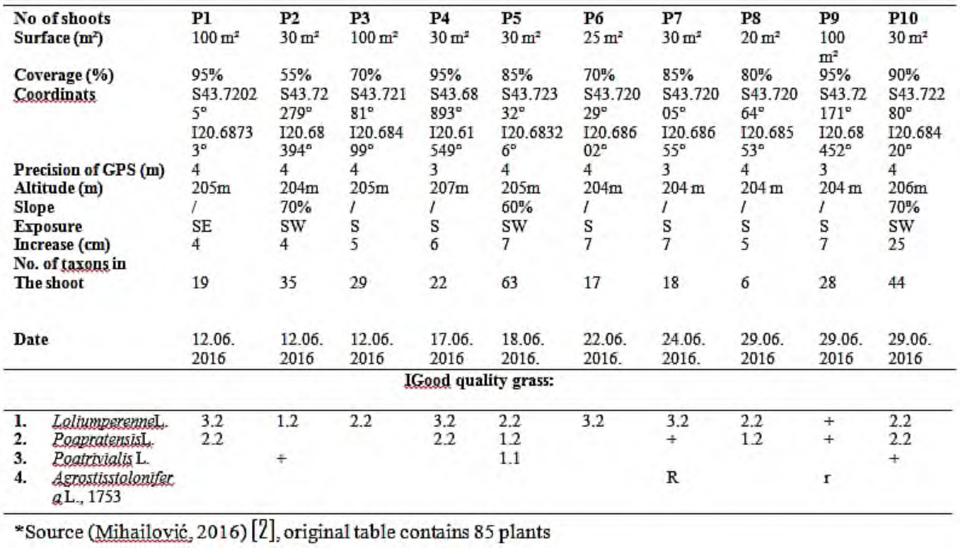


Genera	**No. of species**	**Percentage (%)**
Rumex L.	5	6
Poa L.	4	5
Trifolium L.	3	3,5
Plantago L.	3	3,5
Medicago L.	2	2,3
Polygonum L.	2	2,3
Carex L.	2	2,3
Sonchus L.	2	2,3
Ukupno	23	27,2

Among the most frequent families in the studied areas are tribes *Rumex* L., *Trifolium* L. and *Poa* L. from which usually lawns are based and on surfaces that have a low intensity of care and maintenance are represented genera *Medicago* L., *Sonchus* L. [2]. Among the represented families there is a rod *Carex* L. that is as pointed out by Stavretović [12], widespread in Serbia and it is common species in humid localities, flooded and clayey grounds. In the studied surfaces are present and representatives of ruderal drier habitats *Polygonum* L., *Plantago* L., *Arctium* L., *Cirsium* Mill [2]. The most abundant species in the grass areas of Ibar Quay are: *Lolium perenne* L., *Cynodon dactylon* L., *Plantago lanceolata* L. and *Poa pratensis* L. By analyzing the presence of genera of our research and comparing with the research of the quays (Petrovic, 2015) [14], and pastures urban Belgrade (Stavretović, 2002) [15] it can be seen similarity. Covering of the soil at the researched areas are of the order of 55% (minimum) to 95% (maximum) [2]. The highest coverage was recorded in areas with a high prevalence of high-quality grass. Average height of the pitch in the certain area, is 7.7 cm [2].

The largest number of plant species was noted in the lawns of the inclination, on the grass surface which is marked with the ordinal number 5, wererecorded in 63 plant species, on the surface 10. were recorded in 44 plant species. While on the grass surface number 8.theleast number of plants was recorded, 6 plant species *(Lolium* *perenne* L., *Poa pratensis* L., *Cynodon dactylon* L., *Trifolium repens* L., *Taraxacum officinale* (L.) Weber ex FH Wigg., *Plantago major* L.), which is a reflection of the conditions of the environment and exposure of the anthropogenic factor [2] (Table 3).

Table 3. Short table of fitoceonologic shoots of lawns of Ibar quay**,** with the presentation of the first categorie **Good quality**



No of shoots	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**
Surface (m^2)	100 m^2	30 m^2	100 m^2	30 m^2	30 m^2	25 m^2	30 m^2	20 m^2	100 m^2	30 m^2
Coverage (%)	95%	55%	70%	95%	85%	70%	85%	80%	95%	90%
Coordinats	S43.72025° I20.68733°	S43.72279° I20.68394°	S43.72181° I20.68499°	S43.68893° I20.61549°	S43.72332° I20.68326°	S43.72029° I20.68602°	S43.72005° I20.68655°	S43.72064° I20.68553°	S43.72171° I20.68452°	S43.72280° I20.68420°
Precision of GPS (m)	4	4	4	3	4	4	3	4	3	4
Altitude (m)	205m	204m	205m	207m	205m	204m	204 m	204 m	204 m	206m
Slope	/	70%	/	/	60%	/	/	/	/	70%
Exposure	SE	SW	S	S	SW	S	S	S	S	SW
Increase (cm)	4	4	5	6	7	7	7	5	7	25
No. of taxons in The shoot	19	35	29	22	63	17	18	6	28	44
Date	12.06. 2016	12.06. 2016	12.06. 2016	17.06. 2016	18.06. 2016.	22.06. 2016.	24.06. 2016.	29.06. 2016	29.06. 2016	29.06. 2016
					IGood quality grass:					
1. *LoliumperenneL.*	3.2	1.2	2.2	3.2	2.2	3.2	3.2	2.2	+	2.2
2. *PoapratensisL.*	2.2			2.2	1.2		+	1.2	+	2.2
3. *Poatrivialis* L.		+			1.1					+
4. *Agrostisstolonifera* L., 1753							R		r	

*Source (Mihailović, 2016) [2], original table contains 85 plants

CONCLUSION

Structural analysis of the lawn was comprised of 10 phytocoenological records, in which is recorded, and analyzed 85 plant taxa. In the analyzed flora grass areas there were already 68 genera and 27 families. Site conditions and the specific ambient conditions, in conjunction with climate factors have caused the richness and variety of plant taxa to the studied surface. The largest number of plant species is recorded on grass areas of inclination, on the grass surface which is marked with number 5 are recorded in 63 plant species and on the grass surface which is marked with number 10 there were 44 plant species. While on the grass surface, number 8, at least the plants documented (6 species), which is a reflection of the conditions of the environment and exposure of anthropogenic factor. Species and their number is stated in the grasslands of researched area indicates a low level of care and maintenance of grass areas. On the studied area the most common representatives are those of the family Gramineae Juss. This family is comprised of 17 plant species or 20% of the total number of plants present. To family Compositae Giseke belongs 16 plant species, that is 19% of the total number of plants present, followed by the family of Leguminosae Juss. and Polygonaceae Juss. with 8 plants (9%). Among the most frequent families in the studied areas are the families of the *Rumex* L., *Trifolium* L. and *Poa* L. of which usuallylawnsare based and on surfaces that have a low intensity care and maintenance are represented genera *Medicago* L., *Sonchus*

L., among the represented families there is also genus *Carex* L. In the studied areas, there are also representatives of ruderal habitats drier habitat *Polygonum* L., *Plantago* L., *Arctium* L., *Cirsium* Mill., this situation is a reflection of low intensity, a measure of care and maintenance and exposure to anthropogenic factor.

In order for a lown to be good quality and functional, it is necessary for implementation of care and maintenance to be regularly and timely. Some of the basic measures of care that need to be implemented in the studied areas are regular mowing to reduce the presence and spread of weeds, edging the lawn, removing cut grass, rake the lawn, aerating the lawn, if necessary, correct the cover of the grass areas where you need by overseedingthelawn with high quality species that are suitable for the type of pitch, pitch feeding with organic and mineral fertilizers, irrigation, if necessary, depending of the pitch type, control weeds, pests and diseases.

REFERENCES

1. Stavretović, N., Jovanović, S.: Phytogeographical analysis of the flora of Belgradelawns. Phytologia Balcanica *11(2)*: 185-191, 2005.
2. Mihailović, M.: Analiza zelene površine sportsko-rekreativnog kompleksa na Ibarskom keju u Kraljevu, master rad, Šumarskifakultet, Univerzitet u Beogradu, 2016.
3. Braun-Blanquet, J.: Pflanzensoziologie, Grundzüge der Vegetationskunde, Springer Verlag, Wien-New York, 1964.
4. British Standard BS 7370-3 (1991): Grounds maintenance – Recommendations for maintenance of amenity and functional turf (other than sports turf), The British Standard Institution, UK.
5. Josifović, M., Stjepanović, L., Kojić, M., Diklić, N., (ur.): Flora SR Srbije, I-H, SANU, Beograd, 1970-1986.
6. Šarić, T.: Atlas korova, Zavod za udžbenike, Sarajevo, 1978.
7. Lanzara P.,Pizzetti M.:Drveće, Mladinska knjiga, Ljubljana, 1984.
8. Kojić, M.: Mala korovska flora, Naučna knjiga, Beograd, 1986.
9. Mišić, L., Lakušić, R.: Livadske biljke, Zavod za udžbenike i nastavna sredstva, Beograd, 1990.
10. Javorka, S., Csapody, V.: Iconographia Florae Partis Austro-Orientalis Europae Centralis, Akademiai Kiado, Budapest, 1991.
11. Ocokoljić M., Ninić-Todorović J.:Priručnik iz dekorativne dendrologije, Šumarskifakultet, Beograd, 2003.
12. Stavretović, N.: Kvalitetnevrste i korovi u travnjacima urbanog područja, Unija bioloških naučnih društava Srbije, Beograd, 2008.
13. Jovanović, S.: Ekološka studija ruderalne flore i vegetacije Beograda, doktorska disertacija, Biološkifakultet, Univerzitet u Beogradu, 1994.
14. Petrović, J.: Strukturna, ekološka i sociološka istraživanja travnjaka rekreativnih površina, doktorska disertacija, Šumarskifakultet, Univerzitet u Beogradu, 2015.
15. Stavretović, N.: Struktura travnjaka kao determinator kvaliteta u različitim tipovima travnih površina urbanog područja Beograda, doktorska disertacija, Šumarski fakultet, Univerzitet u Beogradu, 2002.

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THE OBSERVED ECONOMIC VALUES OF ECOSYSTEM SERVICES OF THE PARKS IN THE CITY OF BELGRADE

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ABSTRACT

This paper explores the mutual economic importance of green infrastructure and business. These approaches are a novelty and allow us to test hypotheses regarding the influence that urban green infrastructure as a whole and urban green components individually, have on business activity. The focus of this research is on perceived value and beneficiary awareness, therefore we gathered data concerning café density near parks. We surveyed café owners and customers about the perceived benefits of having green space close by. This study gave a brief assessment of the ecosystem services of the parks on the business productivity of the selected cafés in the city of Belgrade.

Key words: urban green infrastructure, ecosystem services, perceived value, city park, cafés, the city of Belgarade.

INTRODUCTION

Integrated functioning of people and urban ecosystems provides continuous and strong development of socio-economic and ecological values of green infrastructure. Ecosystems services represent a key to sustained survival and well-being to residents in urban areas (1). Although ecosystem services are often assumed as "nature for free" by people, many businesses rely on the opportunity to benefit and value the urban green areas (2, 3). Many urban ecosystem services have direct monetary values as the alternative to some technical solutions such as microclimate regulation. The urban green and blue infrastructure can play a key role increasing the adaptive capacity to cope with climate change especially since such investments generate many other services and contribute to human well-being (4). Investments and development of green infrastructure in urban landscapes can provide multiple monetary and non-monetary benefits to society and offer opportunities for design, installation and maintenance in a form of cafe gardens, restaurants or open markets (5, 6). Urban ecosystem provides services that are generally recognized by a high intensity of demand due to a very large number of immediate local beneficiaries, compared to ecosystem services generated in suburban or rural areas (7). Several studies found that proximity to large parks, urban forests or water

Also, some hedonic pricing studies focused on different types of urban green spaces revealing positive impacts on property prices and other services nearby by isolating the impacts of individual attributes of a service or environmental attribute on their prices (11, 12, 13).

This study refers to the location of the selected cafés as an important social factor when it comes to ecosystem service of the urban green spaces such as the park that can be related to the customers' choice. In order to explore the importance of proximity of urban green space for business and additional benefits, we have conducted the survey among the business owners and managers of cafés to evaluate how does the location of their facilities in the park influence on their business productivity. In this way, we wanted to explore the economic values of ecosystem services provided by parks. This study relied on similar research that was conducted in Berlin in 2015 (14).

METHOD

Survey and location

A pilot study was conducted in the city of Belgrade in three central municipalities Čukarica, Palilula and Stari Grad within which are located three large parks with cafés. The selected cafés are "Park Caffe" (Čukarica), "Caffe Giardino Tas" (Palilula) and "Mali Kalemegan caffe" (Stari Grad) (Figure 1). The cafés were also located in the areas with the high-frequency of different cafés that are set up around the parks or in a mild distance. Although in some of the hedonic pricing studies the value of a property or business productivity did not depend on the size of the nearest green space (15, 16), for this research the parks were an approximately same size and facilities located in them, performed the same type of business. The survey was conducted on four days, including two weekdays during the day between 10-14:00 hours and 14-18:00 hours and each interview lasted approximately 10 min. The three café owners/managers were interviewed and the survey included 5 questions:

1. How long has the café been at this location?
2. Location matters for this kind of business?
3. Do the seasonal variabilities affect the number of guests?
4. Would it be different without the park nearby?
5. Who are your customers?

The café visitors were also interviewed. A survey included 100 café customers. The respondents were selected via systematic sampling in which every second customer was interviewed. Face-to-face a survey for customers included the questions about cafés, park location and overall experience of the venue:

1. Why did you choose this café?
2. Did the location at the park matter for the choice to sit here?
3. What do you like the most at this café?

In order to get a more comprehensive view of the interview location and situation, in addition to these questions the average café incomes, the price of a regular coffee and weather conditions were taken into consideration.

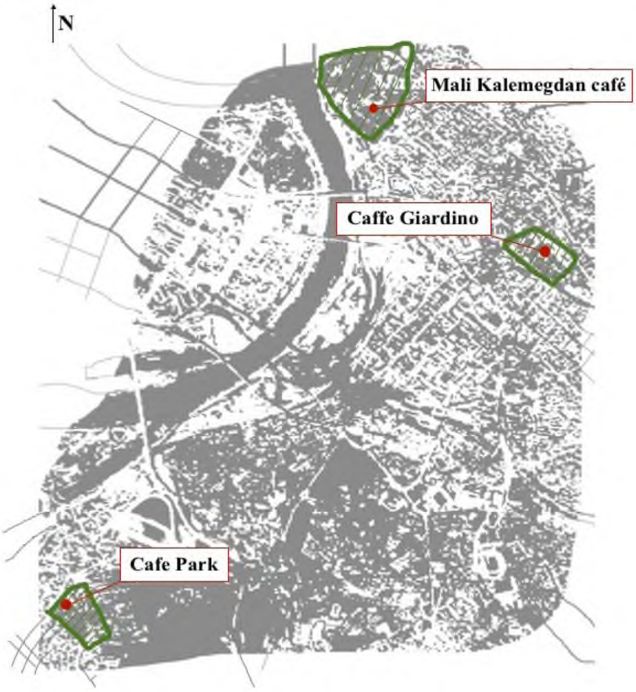

Figure 1. The locations of the cafés in the city of Belgrade

The Park Caffe is located in the Banovo Brdo park, along with the main street in one of the greenest municipalities in the city of Belgrade, the Čukarica municipality (Figure 2). The Cafe Park is established at this location for over the 10 years. The Caffe Giardino Tas is placed in the Tašmajdan park, the big park located in the Palilula municipality, which is one of the central municipalities of the City of Belgrade. The Caffe Giardino Tas is also at this location for over the 10 years and maintains a long tradition in this kind of business (Figure 3). The Mali Kalemegdan caffe is located in the Kalemegdan park, the biggest park in the municipality Stari Grad, with the great historical value (Figure 4).

Figure 2. *"Park Caffe"*

Figure 3. *"Caffe Giardino Tas"*

Figure 4. *"Mali Kalemegdan caffe"*

In order to have a more comprehensive understanding of the researched locations and situation, in addition to the survey questions, the several items were included. The survey was conducted in October 2016. The weather conditions during the interviews were adequate and the cafés were medium busy to very busy with guests. All three cafés offer the average prices of regular coffee.

RESULTS AND DISCUSSION

The results of the survey recorded some differences among the café owners regarding a question about the importance of the park location for establishing their business (Figure 5). The two of three owners agreed that the closeness of the park plays a very important role for a business and café productivity. The common stand was that the parks provide a unique ambiance and make every difference with their presence. The owners and managers in all three cafés noted the relation between the seasonal variabilities and the higher frequency of guests in a period from April to October. This finding can rely on the results of the study conducted in Berlin (14). There were some variations about the types of the café customers and all three owners estimated their quests differently. There was a high score of "locals" in the Park Caffe, noticing that the café in the Čukarica municipality attracts mostly residents from that part of the city. The Caffe Giardino Tas recorded a higher score of "non-locals", mainly students, comparing to the other two cafés. According to the results, the Mali Kalemegdan caffe attracts a high share of international visitors.

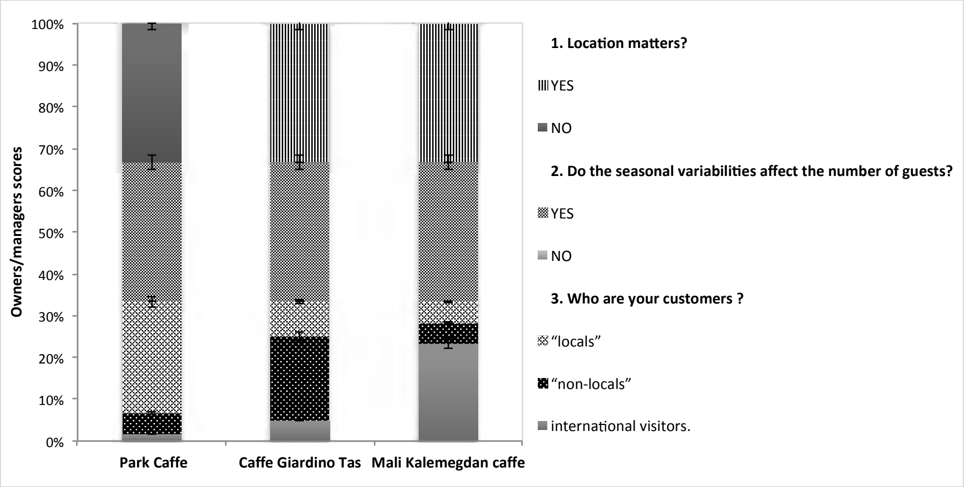

Figure 5. Scores by the café owners and managers regarding the importance of the park location and seasonal variabilities to business productivity (the higher the score, the higher the reported importance of the café location in the park), with estimated scores of different types of café visitors during the season (2016).

The interviewed customers on the question "Why did you choose this café?" expressed different reasons for café selection, giving the higher score to their choice (Figure 6). The visitors of the Caffe Park were regular guests, mostly locals who live nearby the park Banovo Brdo. The Caffe Giardino attracts the customers mainly because of its location in the park Tašmajdan, according to the 70% of respondents. The Mali Kalemegdan caffe holds a high share of the international customers. Around the 60% of the respondents at the Kalemegdan park were tourists who are visiting the capital. The customers in all three cafés agreed that the location of the café in the park is an advantage compared to the other cafés nearby (Figure 7). All respondents unanimously answered that the park surrounding is the fact they like the most when they evaluate the overall experience of the cafés (Figure 8). Using the proximity of green space to express the positive impact on the property value or business productivity can monetary benefit, especially in terms of attracting customers (10, 17).

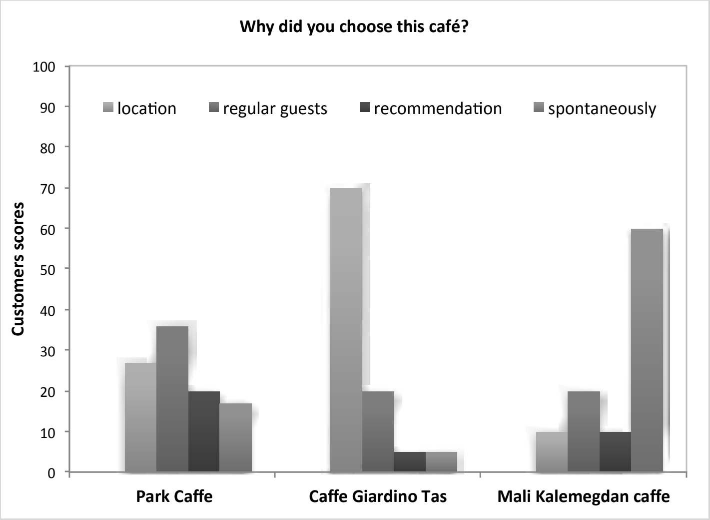

Figure 6. Scores by the customers regarding the reasons for café selection during the season (2016).

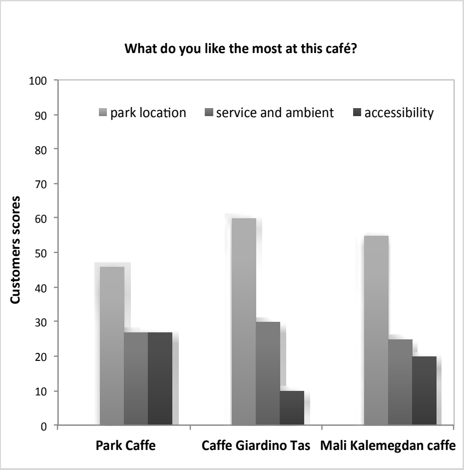

Figure 7.

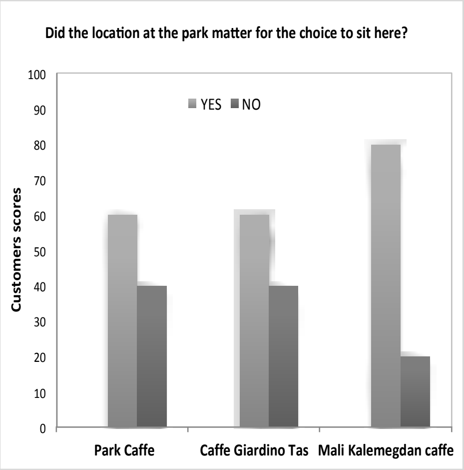

Figure 8.

Figure 7 and 8. Scores by the café customers regarding the importance of the café location in the park (the higher the score, the higher the reported importance of the café location in the park), with estimated scores of the overall experience of the café visitors during the season (2016).

CONCLUSION

This study gave a brief assessment of the ecosystem services of the parks on the business productivity of the selected cafés. The interviewed owners of all three facilities expressed a high importance of the park surrounding and noted that proximity of the park provides additional benefits to their business, regardless if the customers were " locals" or international visitors. They also highlighted the connection of the seasonal variabilities and the higher frequency of guests, explaining that their cafés mainly offer the open-air type of leisure. Although the results of the customer's survey provided the different answers regarding the café selection, the respondents at all three locations agreed that the proximity of the park surely is an advantage. They also pointed out that the park ambient elevates the overall experience of their leisure time.

The social aspect of the ecosystem services, provided by the examined parks, imposed the location as an important economic factor and environmental attribute. The presented differences can reveal interesting trends in this pilot study, but the sample size was not representative enough for any statistically significant result or conclusion. The notable and complete results, with the larger number of cafés and sample size, are to be expected in a more comprehensive study in summer/autumn season 2017.

REFERENCES

1. Millennium Ecosystem Assessment: Living beyond our means: natural assets and human well-being. Island Press, Washington D.C., 2005.
2. Bishop, J. (Ed.): The Economics of Ecosystems and Biodiversity in Business and Enterprise. Routledge, New York and London, 2013.
3. Kronenberg, J.: Environmental impacts of the use of ecosystem services: case study of birdwatching. Environ. Manage, 54 (2014), 617–30. doi:10.1007/s00267-014-0317-8
4. Solecki, W., Marcotullio, PJ.: Climate change and urban biodiversity vulnerability. In Urbanization, Biodiversity and Ecosystem Services: Challenges and Opportunities. Edited by Elmqvist, T., Fragkias, M., Goodness, J., Guneralp, B., Marcotullio, PJ., McDonald, RI., Parnell, S., Schewenius, M., Sendstad, M., Seto, KC. et al.: Springer; 2013:485-504.
5. Werna, E.: Working in Green Cities: Improving the Urban Environment While Creating Jobs and Enhancing Working Conditions, in: Simpson, R., Zimmermann, M. (Eds.), The Economy of Green Cities, Local Sustainability. Springer Netherlands; 2013, 57–70.
6. Elmqvist, T., Fragkias, M., Goodness, J., Guneralp, B., Marcotullio, PJ., McDonald, RI., Parnell, S., Schewenius, M., Sendstad, M., Seto, KC. (Eds): et al.: Urbanization, Biodiversity and Ecosystem Services: Challenges and Opportunities. Springer; 2013.
7. Elmqvist et al.: Benefits of restoring ecosystem services in urban areas. Current Opinion in Environmental Sustainability, 14 (2015), 101–108.

8. Anderson, ST., West, SE.: Open space, residential property values, and spatial context. Regional Science and Urban Economics, 36 (2006), 773–789. http://dx.doi.org/10.1016/j.regsciurbeco.2006.03.007
9. Larson, EK., Perrings, C.: The value of water-related amenities in an arid city: The case of the Phoenix Metropolitan Area. Landscape and Urban Planning, 109 (2013), 45–55. http://dx.doi.org/10.1016/j.landurbplan.2012.10.008
10. Czembrowski, P., Kronenberg, J.: Hedonic pricing and different urban green space types and sizes: Insights into the discussion on valuing ecosystem services. Landscape and Urban Planning, 146 (2016), 11–19.
11. Brander, LM., Koetse, MJ.: The value of urban open space: Meta-analyses of contingent valuation and hedonic pricing results. Journal of Environmental Management, 92 (2011), 2763–2773. http://dx.doi.org/10.1016/j.jenvman.2011.06.019
12. Łowicki, D.: Land prices as an indicator of the recreational services of ecosystems. Ekonomia i Środowisko, 42 (2012), 167–175.
13. Kabisch, N., Haase, D.: Green spaces of European cities revisited for 1990 - 2006. Landscape and Urban Planning, 110 (2013), 113–122. http://dx.doi.org/10. 1016/j.landurbplan.2012.10.017
14. Andersson, E., Kronenberg, J., Haase, D., Strohbach, M., Kabisch, N., Engström, G., Czembrowski, P.: Perceived benefits of close proximity to green space: cafés in Berlin, Case study. Cash flows generated by urban green spaces, WP4. Green Surge, 2015.
15. Bengochea Morancho, A.: A hedonic valuation of urban green areas. Landscape and Urban Planning, 66 (2003), 35–41. http://dx.doi.org/10.1016/S0169-2046(03)00093-8
16. Tyrväinen, L., Miettinen, A.: Property prices and urban forest amenities. Journal of Environmental Economics and Management, 39 (2000), 205–223. http://dx.doi.org/10.1006/jeem.1999.1097
17. Kong, F., Yin, H., Nakagoshi, N.: Using GIS and landscape metrics in the hedonic price modeling of the amenity value of urban green space: A case study in Jinan City, China. Landscape and Urban Planning, 79 (2007), 240–252. http:// dx.doi.org/10.1016/j.landurbplan.2006.02.013

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