PROCEEDINGS

26th International Conference Ecological Truth and Environmental Research

EDITOR
Snežana Šerbula

12-15 June 2018, Hotel Jezero, Bor Lake, Serbia

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26th INTERNATIONAL CONFERENCE

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PREFACE

The rapid development of industry and technology, the increased demand for using fossil fuels and exploitation of primary raw materials call into question sustainability of progress in today's society. Environmental research and ecological truth are the main subjects of the 26th International Conference Ecological Truth & Environmental Research 2018 (EcoTER'18), which will be held at Bor Lake, Serbia, 12-15 June 2018. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

The EcoTER'18 is organized by the Technical faculty in Bor, the University of Belgrade and co-organized by the Faculty of Technology, University of Banja Luka, the Faculty of Metallurgy and Technology, Podgorica, the Faculty of Metallurgy, Sisak and the Society of Young Researchers, Bor.

The primary goal of EcoTER'18 is to bring together academics, researchers, and industry engineers to exchange their experiences, expertise and ideas, and also to consider possibilities for collaborative research.

This year's conference is dedicated to the memory of Professor Zoran Marković, who organized the Conference for many years and who was one of our most loyal and active Committee members.

These proceedings include 77 papers from authors coming from universities, research institutes and industries in 13 countries: Argentina, Poland, Republic of Belarus, Turkey, France, Italia, Romania, Bulgaria, Croatia, Bosnia and Herzegovina, Macedonia, Montenegro, and Serbia.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged. The support of the sponsors and their willingness and ability to cooperate has been of great importance for the success of EcoTER'18. The Organizing Committee would like to extend their appreciation and gratitude to all the sponsors and friends of the Conference for their donations and support.

We would like to thank all the authors who have contributed to these proceedings, and also to the members of the scientific and organizing committees, reviewer, speakers, chairpersons and all the Conference participants for their support to EcoTER'18. Sincere thanks to all the people who have contributed to the successful organization of EcoTER'18.

On behalf of the 26th EcoTER Organizing Committee,

Snežana Šerbula, PhD Full Professor

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Plenary Lectures

APPLICATION OF CHITOSAN IN REMOVAL OF MOLYBDENUM, ARSENIC AND CHROMIUM FROM CONTAMINATED WATER AND GROUNDWATER

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Abstract

Water pollution by heavy metals represents a serious problem around the world. Among various treatment techniques for water remediation, adsorption is an effective and versatile method due to the low cost, effectiveness and simplicity. Chitosan is a cationic polysaccharide with an excellent adsorption capacity of heavy metal ions. Molybdenum is a trace element that is present in plants and animals. Pollution by molybdenum species in water becomes a serious danger to general population. Arsenic is an important environmental element because of its high toxicity at the level of parts per billion. Chromium is a very toxic heavy metal, and it is discharged in the effluents from many industries. The goal of this study was the application of chitosan as a sorbent for Mo(VI), As(V) and Cr(VI) removal. Chitosan has a high adsorption capacity (265 mg molybdate/ g chitosan; 110 mg arsenate/ g chitosan; 211 mg chromate/ g chitosan) at 20 ºC and pH 2.7- 4.5. SEM images showed that morphological surface changes happen after metal adsorption. The results obtained demonstrate the ability of chitosan to remove these toxic ions from water and support further implementation of the system to decontaminate water at higher scale.

Keywords: Chitosan, Molybdenum, Arsenic, Chromium, Groundwater

INTRODUCTION

Heavy metal contamination represents a major problem around the world due to industrial wastewaters discharged into natural water bodies [1]. Some water purification processes have been applied to wastewaters including adsorption, electrolytic chemical treatment, membrane separation and biological treatment. From these techniques, adsorption has some advantages such as low cost, effectiveness and simplicity.

Chitosan is a cationic polysaccharide (poly[β-(1→4)-2-amino-2-deoxy-D-glucopyranose]) partially acetylated at the 2-amino group. It is obtained by deacetylation of chitin, which is a natural polysaccharide component of arthropod and crustacean shells [2]. Chitosan is soluble in acetic acid, and insoluble in dilute sulphuric acid. Presence of free amino and hydroxyl groups in its structure confers to this polysaccharide an excellent adsorption capacity of heavy metals ions [3]. The low cost, non- toxic and biodegradable properties combined to its high adsorption capacity of heavy metals make this polysaccharide an excellent option to be used in treatment of polluted water.

Molybdenum is a trace element that is present in plants and animals [4]. It is harmful to plants at concentration higher than 5 μg/g, and for ruminants at concentration higher than μg/g [5]. Molybdenum has various industrial applications such as constituent of electron and vacuum tubes, fireproof thermal materials and hardness steel alloys [6]. Pollution by molybdenum species in water bodies and groundwater becomes a serious danger to general population if their concentration exceeds 5 mg/L [7,8].

Exposure of humans to naturally high concentrations of As in groundwater is one of the most widespread environmental problems in many countries [9]. Arsenic is found in natural waters and the oxidation states that predominate are As(III), As(V). Arsenic can occur in inorganic and organic forms [10], being the inorganic forms which represent, in general, the greatest toxicity for people. The World Health Organization (WHO) recommended a limit of 10 ppb as the maximum permissible arsenic level.

Chromium is a very toxic heavy metal, and it is discharged in the effluents from many industries, including steel plants, electroplating, tannery, and pigment and dye industries [11]. Most chromium exists in the environment as Cr(VI) and Cr(III). The allowed limit by U.S. EPA for Cr discharged is 0.1 mg/L [12]. Besides, Cr(III) is susceptible to precipitation in soil strata while Cr(VI) is mobile and always leached out by groundwater. Thus, removal of Cr(VI) from wastewater or soil to avoid Cr pollution is a key step when designing environmental friendly processes [13].

The goal of this study was the application of chitosan biopolymer as a sorbent for Mo(VI), As(V) and Cr(VI) removal. Since this polysaccharide is abundant in nature and has a low cost of preparation, it has been selected as a possible biosorbent for treatment of polluted waters.

MATERIALS AND METHODS

Materials

Chitosan (Sigma, p.a.), sodium molybdate dehydrate (Baker, p.a.), sodium arsenate (Biopack, p.a.), ascorbic acid (Sigma, p.a.), sodium thiosulphate pentahydrate (Cicarelli, p.a.), ammonium heptamolybdate tetrahydrate (Sigma, p.a.), antimony potassium tartrate (Sigma, p.a.), sodium nitrate (Cicarelli, p.a.), potassium dichromate (Merck, p.a.), ethanol (Cicarelli, p.a.), 1,5-diphenylcarbazide (Sigma, p.a.), acetic acid (Cicarelli, 98%), sodium hydroxide (Merck, 99%), 1,2-dihydrobenzene (Sigma, p.a.), sodium methabisulfite (Cicarelli, p.a.), were employed as received. MilliQ deionized water was used to prepare aqueous solutions. Chitosan solutions were prepared by dissolving the polysaccharide into 4% w/v acetic acid solution at 50 ºC.

Chitosan characterization

Specific viscosity was determined at 25 °C by an Ostwald-type viscometer. Flow times were recorded with a stopwatch with reproducibility ±0.2 s. Pycnometry technique was used to determine densities of solutions. Chitosan solutions (1.0–5.0 g/L) in 0.10 M acetic acid and 0.2 M NaCl were used in this experiment [14]. The experimental value of intrinsic viscosity was 265.5. Chitosan molecular weight (MW) was obtained applying Mark Houwink–Sakurada equation [15] and the value of MW obtained was 360000 ± 100 g/mol. The determination of degree of acetylation (DA) was performed by ^{1}H NMR [16]. 5.0 mg of chitosan was introduced into a 5 mm NMR test tube and further vacuum dried at 50 °C for 3 h. Then, 0.5 mL of 2.0% DCl/D_20 solution was added, and finally the test tube was kept at 70 °C to dissolve the polymer. The ^{1}H NMR was collected in a Bruker Avance 300 MHz Digital, NS = 64, SW =12.98, O1P= 5.5, Temp: 70 °C. The value of DDA% obtained was 80.2%. pH value at point of zero charge (pHpzc) was determined as described in literature [17]. pHpzc of chitosan was 6.3.

Chitosan gel beads formation

Chitosan gel beads were prepared by dripping a chitosan solution (4% w/v in acetic acid) into a 2.5 M NaOH solution. Freshly prepared chitosan gel beads were left 24 h into NaOH solution and then were separated and washed several times with MilliQ deionized water. An average diameter of 3 mm was obtained for chitosan gel beads.

Statistical experimental design

An experimental screening design was used to identify the key factors that modified significantly the response. A Plackett-Burman design was performed [18]. After the screening design, an optimization design was performed. The optimized model was achieved employing Central Composite Design (CCD) [19]. Analysis of variances (ANOVA) was applied to validate the model.

Batch adsorption experiments

Chitosan was suspended in solutions containing different amounts of Mo(VI), As(V) or Cr(VI). Mo(VI) concentration was determined spectrophotometrically at 400 nm employing catechol in basic media [20], As(V) concentration was determined spectrophotometrically molybdenum blue method [21] and Cr(VI) concentration was determined spectrophotometrically at 540 nm employing 1,5-diphenylcarbazide in acid media [22].

Kinetic and thermodynamic studies were performed at controlled temperature values. Heavy metal removal (q, mg/g) was calculated by Eq. (1):

$$q = (C_0 - C_t)\ V/m \qquad (1)$$

where C_0 and C_t are the heavy metal concentration in solution (mg/L) at time 0 and t, respectively, V is the batch volume (L) and m is the quantity of chitosan used (g).

Continuous adsorption experiments

The adsorption of Mo(VI), As(V) or Cr(VI) by chitosan packed in polypropylene columns of 15 cm long and 1.4 cm of internal diameter was studied. Powder Chitosan was previously equilibrated at working pH, and packed by gravity into the columns keeping constant the package density. Upward flow was used. Solution containing different amounts of heavy metal contaminants was pumped through the columns at room temperature. Samples of 2.0 mL were taken at different time intervals and heavy metal concentration was measured. The column bed performance was described through a breakthrough curve, which was obtained by plotting C/C_0 against time. Breakthrough time (tb, min) was defined for an effluent of 5.0 mg/L of contaminant. Saturation time (tsat, min) was considered when $C/C_0 = 0.95$.

Real contaminated water analysis

Groundwater was collected from a hand pump attached tube well (depth: ∼150 ft) of Buenos Aires and Santa Fe States, Argentina and analysed by standard methods [22]. The parameters analysed (mg/L) were total hardness (1778.51), calcium (492.81), sulphate (1285.7), phosphate (0.118), nitrate (40.3), nitrite (0.053), ammonia (0.00763), organic matter (1.96), total arsenic (0.00574), total chromium (0.2115), chromium(VI) (0.2110), molybdenum (VI) (less than 0.001) and pH (7.80). This water sample was spiked with Mo(VI) up to a level of desire (40.0 mg/L) for conducting experiments and the working pH was adjusted to 2.7. The employed bed depth was 0.9 cm with an upward flow of 9.0 mL/min groundwater. Desorption studies employed 0.10 M solution of NaOH eluent and an upward flow of 2.0 mL/min. The adsorption–desorption cycles were repeated two times.

Spectroscopic characterization

Chitosan beads loaded and unloaded with heavy metal ions were desiccated under vacuum for 48 h until constant mass was obtained. These beads were used in Fourier transformed infrared (FT-IR) analysis, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDS) analysis, Electronic paramagnetic resonance (EPR) spectroscopy and thermogravimetric analysis (TGA) experiments. FT-IR spectra were measured using a Perkin Elmer FT-IR Spectrum One spectrophotometer in the range of 500–4000 cm^{-1} employing KBr pellets. Surface structure of chitosan gel beads was analysed by SEM and Mo, As and Cr adsorbed on the chitosan beads was checked by EDS microanalysis. SEM analysis was performed by means of a FEI QUANTA 200F in low vacuum mode (0.20–0.40 mbar chamber pressure), working distance 10–12 mm, acceleration voltage 10–15 kV, on non- coated samples. Before the analysis, chitosan beads were placed on aluminium stubs by using carbon adhesive disks. Energy Dispersive X-ray (EDS) analysis was performed on the above described SEM apparatus, using a EDAX Si/Li detector, in low vacuum mode, working distance 10 mm, acceleration voltage 30 kV. SEM and EDS analysis were performed at LM CCT Rosario Laboratory. EPR spectra of soy hulls treated with Cr(VI) at different contact times were obtained with a Bruker ESP 300 E computer-controlled spectrometer operating at X-band frequencies (~9.4- 9.8 GHz). Microwave generation was by means of a klystron (ER041MR) and frequencies were measured with a built-in frequency-counter. Spectra were recorded as first derivatives of the microwave absorption in 1024 points at 288 K, using 10 mW microwave power and 100 kHz modulation frequency. g-values were determined by reference to dpph (giso = 2.0036) as an external standard. TGA were performed in Thermogravimetric equipment DTG-60H, Shimadzu, made in Japan. N/P 346-68700-93, atmosphere: air, flow rate: 50 mL/min, temperature range 30-650 °C, temperature rate: 10 °C/min.

RESULTS AND DISCUSSION

Kinetic studies

Rate studies of adsorption processes allow design continuous bed adsorption system [23]. Pseudo first and pseudo second kinetic models were used in the present work to fit adsorption kinetic data. The validity of the model was checked by correlation parameter (R^2). For Mo(VI) sorption, the pseudo-second order kinetic model was the better model to describe experimental kinetic data, with a kinetic constant kads = 0.0046 g min^{-1} mg^{-1} at 20 ºC. Kinetic of As(V) sorption by chitosan was fast at room temperature, so kinetic experiments were performed at 5 ºC. Best fit of experimental data were obtained by the pseudo- first order with a kinetic constant kads = 7.10 min^{-1}. Activation energy (Ea) of adsorption process was calculated from the slope of Arrhenius plot in its linealized form for Mo(VI) sorption [17]. The value of Ea was 8.8 kJ/mol. In physical adsorption, sorbate sorbent equilibrium is rapidly attained and easily reversible, due to forces involved in the process are weak. Ea values for physical adsorption are usually lower than 4.184 kJ/mol, Ea value obtained here was in agreement with a chemisorption mechanism [17,24]. Considering the kinetic experiments results, a chemisorption mechanism was proposed for the removal of Mo(VI) and a physisorption for the removal of As(V) by chitosan.

Adsorption isotherms

Adsorption isotherms were used to describe the equilibrium adsorbate- adsorbent and free adsorbate in aqueous phase. Four isotherm models were used in the present work (Langmuir, Freundlich, Sips and Dubinin-Radushkevich). For Mo(VI) sorption, experimental data were fitted well with Langmuir model. Sips exponent (N) was quite close to unity at the three temperature values. This implied that the use of Langmuir isotherm model for this adsorption system is appropriate. The maximum adsorption capacity increases from 265 mg/g at 20 ºC to 474 mg/g at 40 ºC. The good fitting of Langmuir model suggests that the binding sites in the surface are equals and the molybdate anions form a monolayer over the chitosan bead surface. The mean free energy E (kJ/mol) of adsorption were in the range 8.8–11.2 kJ/mol, supporting that adsorption process follows chemical mechanism. For As(V) experimental data were fitted well with Langmuir model. The maximum adsorption capacity was 41.2 mg/g at 20 ºC. The mean free energy E (kJ/mol) of adsorption was 4.46 kJ/mol, supporting that adsorption process follows physical mechanism.

Spectroscopic characterization

FTIR spectra of chitosan, before and after heavy metal removal, were used to find out the functional groups responsible for heavy metal binding. After heavy metal binding by the polysaccharide, some changes in the FT-IR spectra arise. The signal assigned to O-H stretching was shifted and the C-O vibration was strengthened and shifted. No vibrations corresponding to Mo-N, As-N and Cr-N were observed. These results suggest that hydroxyl groups participate in binding of heavy metal ions onto the surface of the polysaccharide.

SEM images were used for chitosan gel beads surface analysis. The dehydrated gel bead is a spherical particle with an approximate 1.8 mm diameter. The surface presented reliefs in a lineal arrangement on the surface. After heavy metal adsorption the dehydrated gel bead retains its spherical form with an approximate 1.5 mm diameter. The surface suffers some changes: the reliefs were shorter and the distribution of the same was irregular. These changes indicate that the surface polysaccharide chains suffer a rearrangement during the adsorption process. These changes were observed in others systems reported in literature [15,16,24]. EDS mapping showed a uniform surface distribution of heavy metal ions onto chitosan gel beads.

Chitosan thermogram showed a loss of water in the range 100-200 °C (19% mass loss) and decomposition of the polymer in the range 200-300 °C (51% mass loss). This behaviour was expected by chitosan polymer and it was reported previously in literature [16]. Chitosan with Mo(VI) loaded thermogram showed a different behaviour. The loss of water occurs in the range 100–210 °C (17% mass loss) but decomposition of the polymer occurs in the range 220–350 °C (29% mass loss). This results point to chitosan beads loaded with molybdate had a better thermal stability than chitosan beads. The resultant residue represents a higher percent of total polymer mass (39% in chitosan beads loaded with molybdate against 20% in chitosan beads). This increment in residue mass was due to presence of sodium molybdate in the residue. Presence of about 19% of sodium molybdate in the residue is in accordance to the original content of molybdate in the beads (255 mg molybdate/g chitosan bead).

EPR spectra of Cr-loaded chitosan at different contact times showed the presence of an oxo-Cr(V)-biomass intermediate at short contact time. At long contact time only a typical broad signal corresponding to Cr(III) was detected, confirming the total reduction of Cr(VI) to Cr(III) onto the chitosan surface.

Fixed bed column studies

Breakthrough curves at three values of bed heights were obtained. Modified dose- response model described better than Thomas model the experimental breakthrough curves. The values of q_{Th} were in agreement with the experimental q values. The values of k_{Th} decreases as bed height increases, suggesting that kinetic became slower at higher column heights values. This trend in k_{Th} values with respect to column bed height was previously reported in literature [25].

Scale-up studies

Scale-up studies were performed applying the bed depth service time (BDST) model [26]. BDST model was validated by inspection of breakthrough curve at 50%. In this condition, the logarithmic term is equal to zero. Good fitting was achieved at 50% breakthrough validating the application of BDST model to the adsorption process of heavy metal by chitosan.

Real sample analysis

Ultimately, we tested chitosan as an adsorbent for heavy metal ions into contaminated groundwater. Adsorbent reusability was checked by conducting adsorption–desorption cycles. The breakthrough time (tb) was 160 min and the volume of water treated (Vb) at breakthrough was 1.44 L in the first cycle. Due to the high affinity of chitosan towards Cr(VI) species at pH 2.7 (also present in groundwater sample), Cr(VI) removal from groundwater was studied. A removal of 100% Cr(VI) was achieved during the two cycles. Desorption/recovery of Mo(VI) from the column was performed with 0.1 M NaOH solution. It was observed that the percentage (%) of Mo(VI) desorption was 100% and the percentage (%) of Cr(VI) desorption was 0% in the first cycle. The volume of desorption solution employed was 0.09 L. Molybdenum breakthrough time (tb) decreased to 55 min in the second cycle (over 75% loss of removal capacity). Loss of removal capacity was probably due to Cr(VI) kept strongly bonded to chitosan blocking active sites for Mo(VI) removal.

Treatment of As(V) polluted groundwater with fixed bed packed with chitosan were also performed. The optimal conditions for As(V) adsorption from groundwater using chitosan as biosorbent were height column 5.94 cm and flowrate 7.83 mL/min. At these conditions, the theoretical maximum removal of As(V) was found to be 68.3%

The effluent water quality suggests that the molybdenum removed water by chitosan could be used for household purposes.

CONCLUSION

We report the application of chitosan polymer, as a sorbent of Mo(VI), As(V) or Cr(VI) ions. Participation of hydroxyl groups in binding of heavy metals at the surface of chitosan was confirmed by FT-IR analysis. Kinetic and thermodynamic parameters confirm that the removal mechanism was chemical adsorption. Continuous adsorption data were analysed applying three models. Application of chitosan in decontamination of real groundwater samples suggest that this polysaccharide is a good option to be used for household purposes. The high value of qmax and the low cost of this polysaccharide make this biomass a good sorbent for being used in continuous treatment of groundwater and effluents contaminated with toxic anions.

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RESEARCH ON TRACE ELEMENT BIOINDICATION AND AIR POLLUTION TOLERANCE INDEX FROM POLISH BIOLOGIST' PERSPECTIVE

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Abstract

Bioindication study using herbaceous and woody plants was performed in some cities of southern part of Poland in Silesia region. Selected heavy metal contents and physiological parameters in the studied plant leaves of birch (Betula pendula), black locust (Robinia pseudoacacia), plantains species: Plantago lanceolata and P. major, dandelion (Taraxacum officinale) were analysed and compaired for environmental risk assessment. Accumulation capacity of the plants varied in the investigated cities. Average concentration of Zn was the highest in birch leves in Dąbrowa Górnicza. Average concentrations of Fe, Cd and Pb were the highest in Bytom and Pszczyna in P. major. In terms of APTI levels (Air Pollution Tolerance Index) which is a combination of physiological parameters such as chlorophyll content, ascorbic acid content, relative water content (RWC) and leaf extract pH, the most tolerant, were T. officinale and B. pendula, which should be taken into account in protecting urban areas against harmful pollutants, including heavy metals. Other plants can be indicative of urban air and soil contamination. The obtained results can be useful in environmental risk assessment.

Keywords: Trace elements, Bioindication, Air pollution, Tolerance index

INTRODUCTION

The living environment of humans is dominated by urban areas. Both the soil and air in these areas have elevated concentrations of heavy metals, emitted mainly by industrial plants and industrial production, fossil fuel combustion and road traffic. In literature the term "heavy metals" is often replaced by "trace metals" in order to include lighter elements e.g. Al (2.6 g cm^{-3}). Some of these elements are known to be necessary for the proper functioning of the human organism (e.g., Zn, Cu, Fe, Mn, Co, Ni), while others are not used in cell metabolism and are toxic to the organism in even minute quantities (e.g., Cd, Pb, Hg and Al) [1-3]. Environmental pollution with trace metals is a long term global problem due to their high persistence in the environment, high levels of bioaccumulation, high toxicity and very low environmental degradation. Due to their bioaccumulation in the food chain, these toxic elements are a threat to all living organisms, not just humans. The problem of increasing concentrations of heavy metals mainly concerns the landfills of mining and metallurgical wastes, as well as the vicinity of the smelters [4,5]. Such areas are common in the Silesian Voivodship, a region in the southern part of Poland, the main study area of the research.This area is characterized by points of concentrated industry, mainly coal and metallurgical industries, and is associated with the presence of mining and metallurgical landfills. Identification of the ecosystem status, biotic and abiotic parameters, and anthropogenic influences is possible due to observations and studies of living organisms – bioindicators, e.g. on the basis of their quantitative and qualitative characteristics [6]. Monitoring the quality of the environment using plants is also widely accepted as a reliable and inexpensive way of obtaining information on heavy metal pollution. Contaminated sites can be considered as reservoirs of native plants which tolerate and accumulate heavy metals to different degrees. Native plant species, very often ruderal, which are first to colonize contaminated sites, may be valuable bioindicators and bioaccumulators of heavy metals in contaminated areas [4]. The research used *Robinia pseudoacacia*, *Betula pendula*, *Plantago lanceolate*, *P. major*, *Taraxacum officinale* as plant species most commonly encountered in parks and roadsides in the analyzed urban biotopes. These species have been analyzed during similar bioindication studies [2,3,5,7,8]. Plants from the urban environment exposed to pollution exhibit varied responses in the process of photosynthesis, respiration, enzymatic reactions, dysfunction of stoma and cell membrane imbalance [9]. Biomonitoring based on plant leaves has recently been recognized as a thrust area in the field of particulate matter science [2,9]. Plants exposed to environmental pollutants (e.g. heavy metals) absorb, accumulate and integrate these pollutants into their systems [10]. As a combination of plant physiological parameters such as chlorophyll content, ascorbic acid content, relative water content (RWC) and leaf extract pH, the air pollution tolerance index (APTI) seem to be more suitable for ecophysiological research than individual indicators because plants show different responses to different pollutants [11]. The main goals of the research included the assessment of the bioindicative potential of the selected plant species in polluted urban areas and their usefulness in estimating environmental risks based on element accumulation and index APTI; identification of plant species suitable for use in revitalization processes, planning of green areas in polluted urban areas.

MATERIALS AND METHODS

Study area

Dąbrowa Górnicza, Sosnowiec, Katowice, Bytom and Pszczyna are cities in the southern part of Poland in Upper Silesia (Figure 1), a known industrial region of the country. According to Silesian air monitoring data, the average levels of air pollutants (as PM_{10}, $PM_{2.5}$) in the urban areas where plant samples were taken are presented in Table 1. The plant sampling sites in the cities were located close to the biggest industrial plants (e.g., the ironwork, coking plant, waste processing plant), as well as by the main roads with heavy traffic; then the sites in the parks, housing estates, as well as green areas, with a strictly recreational function.

Plant sampling and analysis of metal concentration in soil and plant samples

The sampling of plant species was performed in mid-June from 2013 to 2017. Three composite leaf samples were taken at each site from all species. The leaves were used for heavy metal determination; they were washed thoroughly with tap water to remove any substrate and dust deposits and then rinsed twice with deionized water, then oven dried at 105°C. Dry weight subsamples 0.25 g were wet digested in HNO_3 at 120°C and then diluted to 25 ml with deionized water [12]. Trace elements (Cd, Pb, Zn, Cu, Fe and Mn) were estimated by flame absorption spectrometry (Thermo Scientific iCE 3500). For assurance of the quality of substrate analysis, the procedures were performed on blank samples and on certified reference material (Certified Reference MaterialCTA-OTL-1 Oriental Tobacco Leaves, Department of Analytical Chemistry, Institute of Nuclear Chemistry and Technology, Poland).

Figure 1 *Location map of sampling sites*

Analysis of biochemical parameters of the plants

The Air Pollution Index study (APTI) based on chlorophyll content, ascorbic acid, relative water content and leaf pH may be used in estimating plant tolerance to pollution. The relative leaf water content (RWC) was analysed according to Pathak *et al.* [13]. The total chlorophyll content in fresh leaves (mg g^{-1} f.w.) was determined following the method of Arnon [14].The pH of the leaves was determined with a pH meter by homogenizing 5 g f.w. of leaves in 10 ml of deionized water. The ascorbic acid content of leaf sample was determined according to method given in Keller and Schwanger [15]. Ascorbic acid content, leaf extract pH, total chlorophyll content and relative water content were taken into the following expression (1):

$$APTI\ (Air\ Pollution\ Tolerance\ Index) = \frac{A(T+P)+R}{10} \quad (1)$$

where A is the ascorbic acid content in mg g^{-1} f.w., P is the pH of leaf extract, and R is the relative water content in % [16].

RESULTS AND DISCUSSION

The selected heavy metal concentrations are shown in Table 1. Our study revealed that the accumulation capacity of herbaceous and woody plants varied between the investigated cities. The average concentration of Zn was the highest in the leaves of wood species – *B. pendula* in Dąbrowa Górnicza. Average contents of a microelement Fe and trace elements such as Cd and Pb were the highest in a herbaceous species *Plantago major* in Bytom and in Pszczyna. The highest concentrations of the studied heavy metals were found near Arcelor Mittal Poland smelter, the "Przyjaźń" coking plant, landfills or high traffic sites in Dąbrowa Górnicza, as well as within housing estates in Pszczyna or in parks in Bytom (especially Zn and Cd).

Table 1 *Trace metal concentration in the leaves of studied species within the cities, APTI values and annual mean of $PM_{2.5}$, PM_{10}*

City / species	**Selected trace metal concentration in the leaves of studied species within the cities [mg kg^{-1}]**								**APTI**		**$PM_{2.5}$ [μg m^{-3}]**	**PM_{10} [μg m^{-3}]**	
	Zn		**Fe**		**Cd**		**Pb**						
Dąbrowa Górnicza	min	max	min	max	min	max	min	max	min	max	32	min	max
Robinia pseudoacacia	36.5	67.9	68.1	444.79	0.42	0.9	5.2	29.33	12.8	15.29		22	79
mean	52.72		192.11		0.65		11.08		14.2			mean	46
Betula pendula	min	max	min	max	min	max	min	max	min	max			
	288.3	511	131	456.31	0.17	2.4	2.96	78.87	16	24.11			
mean	389		192.11		0.65		16.02		19.05				
Taraxacum officinale	min	max	min	max	min	max	min	max	min	max			
	94.28	260	81.3	252.78	0.43	2.7	3.18	51.25	24.2	46.6			
mean	179.8		159.18		1.29		28.07		30.97				
Plantago lanceolata	min	max	min	max	min	max	min	max	min	max			
	50.93	145	93.1	549.33	0.92	2.6	8.56	62.5	8.43	14.57			
mean	97.62		299.05		1.55		25.38		11.9				
Sosnowiec	min	max	min	max	min	max	min	max	min	max	33	min	max
Plantago lanceolata	27.7	79.5	69.4	381	0.47	3.1	11.1	32.4	5.19	9.39		21	71
mean	43.24		164.32		1.65		11.44		7.28			mean	39
Robinia pseudoacacia	min	max	min	max	min	max	min	max	min	max			
	21.8	46.7	7.01	136.4	0.25	2.3	5.01	29.09	4.7	7.86			
mean	33.7		95.19		1.41		11.91		7.16				
Katowice	min	max	min	max	min	max	min	max	min	max	35	min	max
Plantago major	62.9	120	111	433.01	0.54	3	12.6	86.97	5.45	8.04		23	66
mean	87.86		198.98		1.38		41.34		6.48			mean	39
Pszczyna	min	max	min	max	min	max	min	max	min	max	43	min	max
Plantago major	39.98	278	126	417.42	0.87	5.9	20.7	85.41	7.3	10.8		26	105
mean	92.11		214.2		3.47		48.47		8.05			mean	52
Bytom	min	max	min	max	min	max	min	max	min	max	35	min	max
Plantago major	112.1	255	255	709.9	0.73	3.8	14.6	24.86	7.43	8.92		18	87
mean	156.48		481.29		1.74		16.43		8.45			mean	43
Toxic concentration [mg kg^{-1}] [1]	100-400		-		5-30		30-300				WHO guide-line limits for annual mean of $PM_{2.5}$ are 10 μg m^{-3}	mean allowable PM_{10} level for 1 year	30
Sufficient or normal concentration [mg kg^{-1}] [1]	27-150		-		0.05-0.2		5-10						

The highest concentrations of the studied metals in Katowice were found in the leaves of *P. major* in the nearest vicinity of non-ferrous plant “Szopienice”, as well as near a former heap of metallurgical wastes in the Wełnowiec district. The elevated concentrations of the studied metals were found in the leaves of plants collected near the roads with high traffic.

The obtained concentrations of the investigated metals in leaves were compared to thresholds considered as toxic for plant tissues (Table 2). Zn concentrations (especially in Dąbrowa, Pszczyna and Bytom) and Pb (occurring in elevated concentration in Dąbrowa Górnicza, Katowice and Pszczyna) were within the ranges considered toxic for plant tissues and above concentrations considered normal for plant tissues. Median concentrations of Zn (220 mg kg^{-1}), Cd (0.28 mg kg^{-1}), Pb (0.33 mg kg^{-1}) and Fe (66 mg kg^{-1}) in birch leaves collected along the north-south highway at the southern tip of Norway from Reimann *et al.* [17] investigations were lower than the average concentration in the birch leaves from Dąbrowa Górnicza. In Massa *et al.* [4] investigation in Italy *P. lanceolata* accumulated lower amounts of Zn, Pb and Cd (40.1-62.5 mg kg^{-1}, 0.6-1.5 mg kg^{-1}, 0.1-0.2 mg kg^{-1}, respectively) than plantain from our study in Dąbrowa Górnicza and Sosnowiec, as well as similar species *P. major* in Katowice, Pszczyna and Bytom. Zn content from *T. officinale* from Dąbrowa Górnicza was higher than in Pisa (~40-145 mg kg^{-1}) [18]. A study from Pisa [19] revealed lower average amounts of Zn (117 mg kg^{-1}) than in our study. For *T. officinale* from Islamabad (Pakistan) (19.1; 14.2; 0.4 mg kg^{-1} respectively) [20] lower accumulated concentrations of Zn, Pb and Cd were shown than in Dąbrowa Górnicza in this plant species.

Diverse physiological parameters are used to determine tolerance to air pollution [9]. Elevated concentrations of ascorbic acid were found in the leaves of plants in traffic-related areas, as well as in the case of *T. officinale* with biotopes affected by industry. Plants with a higher pH were more tolerant to air pollution, which was more pronounced for *T. officinale*. The studied plant species exhibited similar relative water content. A higher total chlorophyll content was also observed in the leaves of plants occurring in parks and roadsides than in the areas affected by industrial emissions (data not shown) [10,21]. Ecophysiological indicators such as chlorophyll content, ascorbic acid, relative water content (RWC) and leaf extract pH are combined in the APTI. With APTI, researchers can indicate plant species resistant to urban pollution [16,22]. APTI studies use trees and shrubs (both deciduous and evergreen) and herbaceous plants [9,11,22]. Average and thresholds APTIs within the studied cities were as follows: *P. lanceolata* 7.28-11.9, *P. major* 6.48-8.45, *R. pseudoacacia* 14.2, *B. pendula* 19.5, *T. officinale* 30.97. Due to the fact that the sensitivity and response of plants to air pollution differ, plant species that are more sensitive may be used as bioindicators of air pollutants, while tolerant species, according to the APTI indicator, may be useful for the planning of efficient green belts [11,23]. According to Padmavathi *et al.* [24] plants with an APTI greater than 17, i.e. *B. pendula* and *T. officinale*, can be used as a barrier against significant urban air and soil pollution. In turn *Robinia pseudoacacia* should be considered as plants with an intermediate tolerance (APTI between 12 and 16). The plantain species such as *P. lanceolata* and *P. major* should be considered as sensitive plants to air pollution and could be used as indicator plant.

CONCLUSION

Our results indicate that the studied plant species can grow in urban polluted areas. However, the contamination alters their physiological parameters. The investigated species varied in studied heavy metal accumulation capability. The highest metal accumulation capability was recorded for *B. pendula*, *T. officinale* and *P. major*. The plants with APTI >17: *B. pendula* and *T. officinale* are suitable as barrier areas for atmospheric pollution. However, other plant species with lower APTI index values can be used as indicators of urban air contamination. The native plants which tolerate and accumulate heavy metals to different degrees may be used to complement physical and chemical analyses in environmental risks assessment.

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TWENTY-FIVE YEARS OF ECOLOGICAL TRUTH

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Abstract

On the occasion of June 5, the World Environment Day (WED), in 1993, the first ecological symposium "Our ecological truth" was organized in Zajecar. The main goal of this meeting is conceived as the possibility to start activities and discussions on ecology and ecological problems in the conditions of war and social crisis, poverty and scarcity of every kind. Soon after its establishment, "Our ecological truth" slowly transformed into the ecological movement of the Timocka Krajina. It has become a major driver of environmental activities in the political, scientific, professional and social level. In the last two and a half decades, "Ecological truth" has evolved and gone through various phases: from a national meeting to an international conference. Ecological truth has its own mission, which meets every year. Its strength is reflected in its successful living and being held every year in the 21st century. One of the basic tasks of the author of this lecture is an analysis of the achieved results in the period from 1993 to 2017.

Keywords: WED, 1993, Conference, Ecology, Twenty-five years, 2017

INTRODUCTION

Preparing for this lecture, the authors were considering whether the twenty-five years of the continuous duration of the "Ecological Truth" was a long enough time to cast a glance back and to find out which one of the benefits of such a scientific conference of international reputation was used, and how far the development of ecological idea has gone and which way it should go further. Furthermore, is something like that so necessary at all today, when the "Ecological Truth" continues its way on, as before?

For the first time, such a backward look was made after ten such conferences [1]. It was quite a lot of work that needed to be done: regarding the definition of ecology and harmonization of ecological terms and concepts, expert-methodological and essential approach to ecology as a science and the possibilities of its use in everyday life.

Ecology is a young science, with an interesting history. The term "ecology" was first used by Ernst Hekel, a follower of the great Darwin, defining it through the relations with the surrounding environment including, in the broadest sense of the word, all the existential relationships of living beings and the environment [2]. Ecology is the science of life, which provides the scientific basis for the protection of nature.

The term human ecology is also used, most often when it comes to ecological analyzes and activities that go hand in hand with the leading political elites and modern economies and their institutions, in order to maintain production that is harmful to the environment and when it wants to maintain an environmentally harmful order - homo tehnicusa [3].

The definition of ecology and functioning of the ecosystem is also found in the "Framework of Life" [4] of our scientist Sinisa Stankovic, born in Zajecar.

WHAT PRECEDED THE ECOLOGICAL TRUTH?

Hygiene - medical ecology

In the sixties of the last century, at the time when the development of industrialization took place, it was necessary, within the framework of the program of "reconstruction and development of socialism" in Yugoslavia, to build factories, restore mines, build electric power plants, railways and roads in the Timok region, to restore the economy as a whole, and to increase the production especially in Bor and Majdanpek. We will here also mention the impacts on the nature, life and health of the population that were created by the construction of the HPP "Djerdap I", where the interventions on the Danube and the coast were such that they significantly influenced the flora, fauna and population both on our and Romania's side. At that time, the ecological fate of this area was altered.

At that time, the Institute of Hygiene in Zajecar was founded with a purpose to monitor the impact of the environment on human health, at first, in industrial plants, and later to spread out, to control the impact of air, noise, lighting and temperature in the manufacturing plants on the health of workers, and later the quality of toxic gases and wastewater from industrial plants and other harmful effects on the environment. Doctors were sent to specialize hygiene, a medical science with attributes of medical ecology. The institute was equipped with adequate equipment, it employed technicians, chemists and toxicologists and gave the first results regarding the state of the environment in the Timocka Krajina area.

Bor mine - the biggest polluter of the environment in Yugoslavia

The results of laboratory investigations of the quality of air, watercourses and soil clearly show that in the seventies, Bor and his surroundings were the most polluted and most devastated space in Yugoslavia. The Timok river became a collector of industrial waters of the Bor copper mine, in which every form of life ceased to exist. It should be said that the Timok river was at the same time a collector of wastewaters from the industry and cities of Knjazevac, Zajecar and Boljevac. During the spring floods, the Timok was poisoned by poisonous pyrites and permanently destroyed fertile soil from the Vrazogrnac river to its confluence in the Danube from year to year. The peasants from Brusnik, Bracevac, Tamnica, Rajac, Rogljevo and Kovilovo have remained without more than a thousand hectares of fertile land. The peasants from the Bulgarian villages, downstream of Bregovo, suffered damage too.

As far as the Bor mine is concerned, in all the reports and analyzes, which always had the significance of the political message, there were always just praises. *No harmful impacts on the environment, nor a proposal for measures to stop further degradation of nature and sanitize the consequences.* A similar situation was in Majdanpek. The Country needed copper and gold. The political and economic elites in Yugoslavia were satisfied.

Ecological incidents, rebellions and meetings

The peasants, who were partly miners in nearby mines and factories in the cities nearby, weren't satisfied with the progress of industry and mining in the Timok region. After World War I, the development of mining in this region caused the degradation of the land and the great dissatisfaction of the population due to such destruction of nature and fertile soil. It was the reason for the peasants' rebellions in the surrounding of Bor, below Rtanj and in the vicinity of Vine. Thus, the "Bulletin of the Moravian Banovina Chamber of Commerce" published in the number 3, January 1, 1939, the following article: *"The coal mine Rtanj* *discharges its coal mine black water in the Mirovstica River, and further into the Black River. From polluted water, the fish died and the animals were killed, especially during drought. Taking this into account, our chamber has threatened the Ministry of Forests, Mines and Banks, asking to protect the interests of agriculture in this region [5]".*

Much worse situation was in the vicinity of Bor and along the Bor river and in the vicinity of other mining and industrial plants between the two wars. On May 7, 1935, the following was written about the rebellion of peasants from the Bor region in the Letopis Bor Parrohi and the Church: *„On that day, peasants from Bor, Slatina, Krivelj, Ostrelj, Brestovac, Bucje, Metovnica and Bela Reka, with skillful concentration and sudden attack, stopped the operation of the copper smelter in the Bor mine after they had beaten some of the personnel in the smelter and banned the work. They were desperate and forced to do it because of the destructive effect of poisonous smoke from the smelter on their crops, soil and cattle. From that day till the 31st of May the smelter did not work, so there was the grace to watch the plants develop and the fields covered by greenery. In the absence of toxic smoke from the smelter, farmers' crops began to progress and even some birds that had not existed before appeared, and with their tweetment, gave life and joy to nature. But on June 1, the Smelter started working again and the smoke from it began to cover, with the fading death, trees, grass, fields, and even the birds under its influence were expelled. - Ah! When will the poisonous effect of this smoke finaly disappear ? When the righteous desire of the peasant will be fulfilled, that the smoke does not destroy the soil, his cattle and his health! [6]".*

After the demolition of a dam on the lake where waste waters and pyrite from the mine in Majdanpek were collected, the village of Debeli Lug and the coastal area flooded to the mouth of the river Pek into the Danube. Residential buildings, stables and yards in Debeli Lug were flooded with toxic wastewater and pyrite, arable land was endangered and living world was destroyed in the water of the Pek River and the Danube.

In the mid-seventies of the 20th century, the communal environment of Zajecar was burdened with industrial pollution from a glass factory, from steam locomotives at the railway station and individual fireplaces. The public was especially harassed by the pollution from industrial plants in the glass factory. In those years, the measurement of air pollution in the communal environment started. After three years of measurement, it was shown that the air was polluted by the contents of the vapor from the glass factory, and it was ordered to take measures to reduce the pollution. There were suggestions that the train station should be moved to another location, thus reducing air pollution by smoke from steam locomotives. This did not happen because they were soon replaced by motor trains. In Bor, the situation was even worse, because the intensity of pollution in the municipal environment of industrial gases was above the maximum allowed concentration every day.

The situation was not improved much, so the population's dissatisfaction led to an ecological meeting in the center of Zajecar in the early 1990s, attended by about 3000 people. A few days later an ecological meeting was organized in Bor, too [7].

Such a public opinion process was inspired by the increased involvement of professional institutions from Zajecar and Bor, in solving the ecological crisis in the Timocka Krajina area and establishing an environmental tribune "Ecological Truth".

Figure 1 *Ecological meetings in Zajecar and Bor*

The Stockholm Conference in 1972 and her echo in the Timocka Krajina

The first United Nations Conference on the Human Environment was held in Stockholm in 1972. This Stockholm Conference marked a milestone in the relationship between humanity and the environment. The first day of the Conference in Stockholm, June 5, was proclaimed World Environment Day (WED). From this Conference, a malicious, apocalyptic message spreads, that if the pollution and destruction of nature, continues at the same pace, life on earth will disappear in the next 50 years! Warning alarm was on as a reminder that natural resources can not be exploited uncontrolled and excessively without consequences for the overall humanity is included. In the focus of interest, The "polluters", that are protected by politics, were found in the focus of interest in the whole of the Timok River basin, and across the hill, in Majdanpek. Cadastres of polluters were being made rapidly. At first, the state was satisfied that "polluters" were paying expensive ecological taxes, because of the damage they do on nature. Problems for solving are very complex and expensive for interventions on obsolete technologies and doing their harmful effect to nature more tolerable. The problems caused by the development of all cities and the urbanization of the Timocka Krajina region should be also added to all this. There was a need for the problems arisen by the intensive industrialization of the Timok region to be restricted by creating institutions and strategies based on science in the field of nature protection from industry and degraded technologies.

Echo of the Conference in Rio in 1992 - new approaches to ecology

The Rio de Janeiro Conference, twenty years after the Stockholm conference, has focused on preserving natural values, especially on biodiversity. While the first was concerned with environmental issues, the other had environmental and developmental issues and was known as the World Earth Summit. The global concept of sustainable development has been officially accepted and adopted at this conference [8].

The Institute for Health Protection "Timok" in Zajecar introduces a new philosophy in the ecology of the Timocka Krajina region, which also reflects on the contents of the work of "Ecological Truth". At the time when this was not taken into account in Serbia, and when many did not know what is biodiversity, the Institute initiated and organized the scientific conference "Our Ecological Truth", thus drawing attention to new approaches to ecology.

The following attitude is taken into account: it is better to protect natural biodiversity more effectively than to lead a war with "polluters". So the issue of ecological education came to the agenda. The results of the research unambiguously indicated low ecological awareness among the population and insufficiently developed health culture.

The Institute offered the school system the Ecological education program, which began to be applied in some secondary schools in Bor and Zajecar. Elementary school in the village of Krivelj had organized for several years "School of ecology" in the village of Gornjane, where pupils of elementary schools from several cities from Serbia and Vojvodina came. The papers about ecological education referenced in a series of scientific conferences of "Ecological Truth" is a proof of the echo the Conference in Rio had in our area.

Community for Science and "Ecological Truth"

Nikola Sainovic started the founding of the Society for Science in Bor in 1986. The first scientific project for the protection of the human environment was related to the so-called. «Floodplain», created after the construction of the hydroelectric power plant "Djerdap I".

Figure 2 *Participants of the "School of ecology" in the village of Gornjane*

It was hosted by several institutions and researchers, led by Academician Vojislav Petrovic, professor of biology, born in Krajina, a former professor of Negotin Gymnasium. Several doctors from the area of the Timok region, who wanted a taste of the eternal grail of science, were also included in a large team of experts of the project. A microbiologist, a toxicologist and a doctor of preventive medicine were engaged in the Institute for Health Protection "Timok" Zajecar, together with the Institute for Copper in Bor and the Technical Faculty in Bor and the Institute seriously began to deal with ecology. We had laws, a science community, institutions, but there was something else missing: an environmental forum where research results, environmental ideas, research approaches, discussions, research and interventions in a damaged nature could be presented. And most importantly, to offer efficient expert solutions to factories and the state and to facilitate the implementation of environmental laws.

What was at first interesting was the fact that researchers began to pay attention to the risks and health-related hazards caused by industry and technology. And not only that.The presence and engagement of the Institute in Zajecar has contributed to the protection of nature with special values: moral, institutional and scientific.

During participation in the work of the Community of Science, Rade Kojdic - Cica, Director of the Institute of Copper Bor, Director of the Institute for Health Protection "Timok" Zajecar, Dr Petar Paunovic, and Toplica Marjanovic from Bor, initiated an initiative for holding a scientific-professional conference "Our Ecological Truth", later "Ecological Truth", today "Ecological Truth and Environmental Research" every year.

The first Conference entitled "Our Ecological Truth", was held on June 5, 1993 in Zajecar. The representatives of the Ministry of Environmental Protection, local governments, businesses, NGOs, the media and doctors of medical centers of the cities in the region of Timocka Krajina took part in the conference. The papers from this scientific conference were published in the Journal "Razvitak" in Zajecar.

Figure 3 *Journal "Razvitak" from 1993*

Our Ecological Truth and Radioactive Waste from Vinca

Soon after its establishment "Our Ecological Truth", slowly began to transform itself into ecological movement of Timocka Krajina region. It has become a serious institution of ecological activities on political, professional and social plan. In the middle of nineties, during a scientific and expert meeting held on Bor Lake, Dr Jordan Aleksic, minister of Ecology and Environmental Protection of the Republic of Serbia, raised a question regarding the radioactive waste from Vinca, having a doubt that the waste had been deposited in the abandoned uranium mine in Kalna [9].

Kladovo Community has initiated the question of the Danube pollution by radionuclides from the waste waters coming from those European countries through which this big river flows. The community was also looking for a solution how to protect vegetable fields from the destruction caused by acid rains that are formed due to air which is pllted by the industrial emissions from the factories in Turn Severin, in neighboring Romania. This opened up a space for researchers and topics that found their place in the programmes of scientific – expert meetings of Ecological Truth.

LEAP - Local Environmental Action Plan

Numerous and varied activities in the field of environmental protection enabled the LEAP - local environmental action plan to be created at the beginning of a new time in 2000, in order to ensure the continuity of human environment protection. The largest number of municipalities in the Timocka Krajina region have made ecological plans under the state's directives, but they have not revived, due to the political and economic crisis. "Ecological truth" continued to live in spite of the war and the mentioned crisis.

TWENTY-FIVE YEARS OF ECOLOGICAL TRUTH

"Ecological Truth" is a traditional scientific-expert conference, today a conference devoted to environment, ecology, public health, sustainable development, and its primary goal is to raise ecological awareness. It has been held for 25 years and, most importantly, it fulfills this mission.

"Ecological Truth" began in 1993 as a national conference, later a national scientific with international participation, and today an international conference. In the past two decades, "Ecological Truth" has been developing and passing through certain phases of its development. However, the milestones in the development of the "Ecological Truth" are the following years: 1994, 1996, 1998, 1999, 2003 and 2010.

In the spring of 1994, the Institute offered cooperation to the Society of Young Researchers and to the Mining and Smelter Basin Bor to jointly continue with the organization of this event. This was one of the crucial moments when the foundations of future organization and cooperation were laid. On this occasion, some strategic decisions were made:

1. "Our Ecological Truth" is to become a multidisciplinary scientific-expert conference on natural values and environmental protection, where the latest scientific, theoretical, expert knowledge and practical experience of experts of different profiles (engineers, doctors, biologists, geographers, free planners , economists, lawyers, pedagogues) will be heard.

2. At the same time, together with the "Ecological Truth", the "Days of Preventive Medicine of Timocka Krajina", which, by then, had already had a five-year tradition of organizing, is to be organized.

3. Apart from the Institute, some other scientific-professional, health and economic organizations as well as non-governmental organizations from Bor and Zajecar will be included in the organization of the Conference.

4. The Conference should become traditional and be organized in all the cities of Timocka Krajina.

According to the number of papers, authors and co-authors, as well as the participants, the second "(Our) Ecological Truth" was the most massive event to date. A Proceeding of abstract papers was prepared for the Conference (up to 2 pages per work).

Every next conference launched some new dilemmas and sought answers to new questions. Preparations for the third conference began with the question: Should such a Conference be organized each year? Do we have enough knowledge, readiness, organizational and financial capabilities? The solution was found in the establishment of cooperation between scientific-professional institutions, economy, local self-government and non-governmental sector, which ensured successful organization.

The next, in 1995, the co-organization of the conference includes the only state higher education institution in the Timocka Krajina region, the Technical faculty in Bor. The Technical faculty in Bor was actively participating in the co-organizing event until 2002, and since 2003, until today, it is the main organizer of the "Ecological Truth", During this period, the Technical faculty in Bor gave a great contribution to the realization of the idea begun in 1993.

In 1996, this scientific conference was named "Ecological Truth" on the proposal Assist. Prof. Dr. Goran Belojevic from the Institute of Hygiene of Medical Science in Belgrade, who was one of his regular participants.

In 1998, it brought some new things, which enriched the content and program of this event and brought it closer to the wider public. From the beginning, one of the basic goals of the Conference was the affirmation of the research work of young people. At the sixth meeting, in 1998, for the first time they had the opportunity to announce their papers to pupils and students within the special section " Scientific youth", and this idea was also accepted at other scientific meetings in Serbia.

The "Ecological Truth" was the only traditional scientific conference organized in wartime in 1999. It was held in Zajecar on the last day of the NATO bombing and on the first day of peace.

Figure 4 *Participants of the "Ecological Truth" in Zajecar, 1999*

Due to the great interest of many experts from the country and abroad, this conference was also developed in 2010, on its 18th birthday, for the first time held as international and for the first time out of East Serbia, in Vojvodina, in Banja Junakovic near Apatin. Accepted works are printed in English in Proceedings. The conference is called the International Conference "Ecological Truth", which is officially used by 2017. The late Prof. Dr. Zoran S. Markovic then stated: *„This is one of the multidisciplinary, international conferences in Serbia that has the official approval of the Ministry of Education, Science and Technological Development.“*

In 2010, from the previous co-organizers, only the Society of Young Researchers from Bor, with the presence of new co-organizers such as: West Backa Administrative District Sombor, Public Health Institute of Sombor, Vojvodina Forest of Sombor, Chamber of Commerce Novi Sad, DP „Agroinstitut“ Sombor, Municipality of Apatin and Sombor City.

Bearing in mind that in the realization and affirmation of the "Ecological Truth", various government, scientific-professional and numerous non-governmental organizations have participated from the very beginning, it is necessary to get acquainted with the nature and basic characteristics of the "Ecological Truth".

The basic characteristics of the Conference "Ecological Truth" are:

- **Science and expertise:** the main goal is the presentation of scientific and professional papers reviewed by the Scientific Committee. All papers were published in special Proceedings, which affirmed the participants and their ecological activities.
- **Multidisciplinarity and interdisciplinarity**: the organizer's desire was to gather experts from different profiles at the same place and to share knowledge about the environment and people's health from the aspect of different sciences, and to point out the possible solutions to the same topic.
- **Actuality and adaptability to the needs of the time:** the number of different topics and sections in which it is dealt is that it is always searched for current scientific aspirations and practical needs of the society. Some sections expanded their scope of work and introduced new sections with contemporary content, for example, Since 2001, there has been a session on the Local Environmental Action Plans (LEAP), which became a special topic at the moment when we began to talk about these plans.
- **Affirmation of research work of young people:** since the first scientific conference special attention has been paid to the affirmation of the research work of young people.
- **Co-operation and capacity building of the local community**: the organization of such an event required the establishment of cooperation of the entire community. One of the goals was to achieve cooperation and strengthen the capacities of all sectors: government (local self-government), business sector, scientific-professional institutions and non-governmental organizations.
- **Publicity:** the conference is seen as an opportunity to inform the public about new scientific knowledge about the environment. Therefore, from the beginning, all the information was available to the media and used every opportunity to talk and write about it.

An analysis of the results achieved at the scientific-professional conference "Ecological truth" is one of the basic tasks of the author of this lecture. Tables 1 to 8 provide statistical analysis of results and events in the period from 1993 to 2017.

The number of published papers at the conference "Ecological Truth" from 1993 to 2017 is given in Tables 1 – 3.

The organizers and co-organizers of the conference "Ecological Truth" from 1993 to 2017 is given in Tables 4 – 6. The venue and the Presidents of the Scientific and Organizing committee of the conference "Ecological Truth" from 1993 to 2017 is given in Table 7. The umber of authors and publications of papers at the conference "Ecological Truth" from 1993 to 2017 is given in table 8, too.

Table 1 *Number of published papers on the national scientific and professional conference "Our Ecological Truth" (1993-2002)*

SESSION	OUR ECOLOGICAL TRUTH										
	Ordinal numbers of Conferences										
	I	II	III	IV	V	VI	VII	VIII	IX	X	∑
EI1. Plenary lectures	10	-	-	-	-	-	-	-	-	-	**10**
EI2. Technology and the state of environment	-	61	55	45	44	26	5	20	22	20	**298**
EI3. Protection and preservation of natural resources	-	33	18	12	20	18	13	21	18	13	**165**
EI4. Ecological education	-	11	11	8	21	6	11	20	10	13	**111**
EI5. Water accumulation – state, problems and perspectives	-	5	7	-	-	-	-	-	-	-	**12**
EI6. Use and water protection	-	-	-	-	-	9	8	8	11	12	**48**
EI7. Food and nutrition of the people	-	13	13	-	-	-	-	-	-	-	**26**
EI8. Nutrition and health								12	10	10	**32**
EI9. Agriculture	-	-	-	-	-	-	10	10	10	8	**38**
EI10. Economy and environmental protection, standardization and homologization of standards	-		6	5	-	-	-	-	-	-	**11**
EI11. Ecological management	-	-	-	-	-	7	2	14	13		**36**
EI12. Urban ecology	-	-	-	-	-	-	5	11	9	20	**45**
EI13. Sustainable tourism	-	-	-	-	-	-	-	-	-	5	**5**
TOTAL EI	**10**	**123**	**110**	**70**	**85**	**66**	**54**	**116**	**103**	**101**	**838**
SESSION	**DAYS OF PREVENTIVE MEDICINE OF TIMOCKA KRAJINA**										
	Ordinal numbers of Conferences										
	6.	**7.**	**8.**	**9.**	**10.**	**11.**	**12.**	**13.**	**14.**	**15.**	**∑**
PM1. Environment and heath	-	12	18	-	-	4	-	-	-	-	**34**
PM2. Energy and health	-	-	-	-	-	-	-	-	4	-	**4**
PM3. Migration and health	-	-	-	2	1	-	-	-	-	-	**3**
PM4. Demographic processes in SRJ	-	-	-	-	-	4	1	6	9	18	**38**
PM5. Preventive medicine	-	-	8	-	-	-	-	-	-	-	**8**
PM6. Preventive medicine in health protection today	-	-	6	-	-	-	-	-	-	-	**6**
PM7. Health of people during the last decade of the XX century	-	-	-	19	-	-	-	-	-	-	**19**
PM8. Prevention and suppression of chronic mass disorders of health – modern achievements	-	-	-	-	-	-	7	11	8	3	**29**
PM9. Social- ecological health model in theory and practice	-	-	-	-	12	7	-	-	-	16	**35**
PM10. Health education and social medicine	-	15	-	-	-	-	-	-	-	-	**15**
PM11. Hygiene	-	30	-	-	-	-	-	-	-	-	**30**
PM12. Epidemiology and microbiology	-	28	-	-	-	-	-	-	-	-	**28**
PM13. Modern ecological-epidemiological approachin solving natural focal infections	-	-	-	3	2	-	-	-	-	-	**5**
PM14. Quality control of immunization	-	-	4	1	-	-	-	-	-	-	**5**
PM15. Lyme, 20 years later	-	11	-	-	-	-	-	-	-	-	**11**
PM16. Microbes and people	-	-	-	9	7	11	6	15	14	7	**69**
TOTAL PM	**0**	**96**	**36**	**34**	**22**	**26**	**14**	**32**	**35**	**44**	**339**
	SPECIAL SESSIONS										
PS1. Scientific and research projects	-	-	-	-	-	4	-	1	1	2	**8**
PS2. National and local ecological action plans	-	-	-	-	-	-	-	-	2	6	**8**
PS3. Scientific youth	-	-	-	-	-	12	-	19	26	31	**88**
TOTAL PS	**0**	**0**	**0**	**0**	**0**	**16**	**0**	**20**	**29**	**39**	**104**
TOTAL PAPERS (EI+PM+PS)	**10**	**219**	**146**	**104**	**107**	**108**	**68**	**168**	**167**	**184**	**1281**

Table 2 *Number of published papers on the scientific and professional conference on natural resources and environmental protection "Ecological Truth" (2003-2009)*

SESSION	SCIENTIFIC AND PROFESSIONAL CONFERENCE ON NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION "ECOLOGICAL TRUTH"							
	Ordinal numbers of Conferences							
	XI	XII	XIII	XIV	XV	XVI	XVII	∑
EI1. Plenary lectures	4	2	1	1	1	1	5	**15**
EI2. Protection and preservation of natural resources	23	16	14	14	14	17	18	**116**
EI3. Technologies, wastes recycling and the environment	22	22	31	28	18	31	-	**152**
EI4. Technological aspects – natural values and their protection	-	-	-	-	-	-	20	**20**
EI5. Nutrition and health	5	5	13	3	5	6	10	**47**
EI6. Agriculture	3	14	11	13	14	12	-	**67**
EI7. Urban ecology	20	15	13	11	14	8	-	**81**
EI8. Air protection	-	-	-	-	-	-	13	**13**
EI9. Water supply and protection	10	10	19	9	7	7	7	**69**
EI10. Land protection	-	-	-	-	-	-	6	**6**
EI11. Energy efficiency	-	-	-	-	-	3	-	**3**
EI12. Waste management and secundary materials recycling	-	-	-	-	12	12	-	**24**
EI13. Ecological management	5	7	8	9	9	5	-	**43**
EI14. Ecological ethics, ecological education, NGO and the environment	8	9	10	6	13	5	-	**51**
EI15. Municipality and environmental protection	-	-	-	-	-	2	26	**28**
EI16. Sustainable development	-	-	-	-	12	7	-	**19**
EI17. Sustainable tourism	5	4	6	16	-	-	-	**31**
EI18. Round table	-	-	-	3	3	3	-	**9**
TOTAL EI	**105**	**104**	**126**	**113**	**122**	**119**	**105**	**794**
SESSION	DAYS OF PREVENTIVE MEDICINE OF TIMOCKA KRAJINA							
	Ordinal numbers of Conferences							
	16.	17.	18.	19.	20.	21.	22.	∑
PM1. Socio-ecological health model in theory and practice	6	2	12	-	6	12	-	**93**
PM2. Prevention and eradication of massive health disorders - the latest developments	3	15		-	5		-	
PM3. Microbes and people (interweaving of macro and micro environment in all spheres of life	5	-	-	-	-		-	
PM4. Demographic processes	14	4	9	-	-		-	
TOTAL PM	**28**	**21**	**21**	**0**	**11**	**12**	**0**	**93**
	SPECIAL SESSIONS							
PS1. Scientific and research projects	-	3	3	2	-	-	-	**16**
PS2. National and local ecological action plans	6	2			-	-	-	
PS3. Scientific youth	16	23	-		4	5	12	**60**
TOTAL PS	**22**	**28**	**3**	**2**	**4**	**5**	**12**	**76**
TOTAL PAPERS (EI+PM+PS)	**155**	**153**	**150**	**115**	**137**	**136**	**117**	**963**

Table 3 *Number of published papers on the International scientific – professional conference "Ecological Truth"(2010-2017)*

SESSION	INTERNATIONAL SCIENTIFIC AND PROFESSIONAL CONFERENCE "ECOLOGICAL TRUTH"								
	Ordinal numbers of Conferences								
	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV	XXV	∑
EI1. Plenary lectures	-	2	2	1	1	4	4	5	**19**
EI2. Protection and preservation of natural resources	10	10	18	10	7	8	7	5	**75**
EI3. Technologies, wastes recycling and the environment	26	26	24	29	30	47	40	31	**253**
EI4. Energy efficiency, environment and climate	6	6	1	5	7	7	8	-	**40**
EI5. Soil and water conservation engineering	10	-	10	13	4	-	19	8	**64**
EI6. Agriculture: agribusiness, agro-engineering and organic food production	5	5	2	-	5	7	8	-	**32**
EI7. Nutrition and health	4	-	1	4	-	-	5	8	**22**
EI8. Urban ecology	5	12	15	6	5	13	-	-	**56**
EI9. Water supply and protection	3	9	-	-	6	4	-	6	**28**
EI10. Ecological management (Law, economy, standardization)	3	6	5	13	13	6	17	7	**70**
EI11. Ecological ethics and ecological education	3	7	3	4	4	6	14	-	**41**
EI12. Environmental ampact assessment	4	1	1	9	5	-	-	19	**39**
EI13. Eco tourism and sustainable development	3	4	4	3	3	7	-	7	**31**
EI14. Preventive medicine and ecology	5	14	4	7	6	7	6	-	**49**
TOTAL EI	**87**	**102**	**90**	**104**	**96**	**116**	**128**	**96**	**819**
					SPECIAL SESSIONS				
PS1. Students' papers	1	6	9	4	-	-	-	-	20
TOTAL PS	**1**	**6**	**9**	**4**	**0**	**0**	**0**	**0**	**20**
TOTAL PAPERS (EI+PS)	**88**	**108**	**99**	**108**	**96**	**116**	**128**	**96**	**839**

Table 4 *Organizers and co-organizers of the national scientific and professional meetings "Our Ecological Truth" (1993-2002)*

ORGANIZER	OUR ECOLOGICAL TRUTH									
	I	II	III	IV	V	VI	VII	VIII	IX	X
University of Belgrade, Technical Faculty in Bor			X	X	X	X	X	X	X	X
Institute for Public Health "Timok" Zajecar	X	X	X	X	X	X	X	X	X	X
Society of Young Researchers Bor		X	X	X	X	X	X	X	X	X
Institute for copper Bor		X						X		
RTB BOR Group		X	X							
Health Center Bor		X	X							
Ministry of Environment and Development SRJ		X								
Ministry of Environmental Protection RS		X								
Community of Negotin						X				
Center for Agricultural Research Zajecar						X	X	X	X	X
Ecological movement "Dubasnica"						X				

Table 5 *Organizers and co-organizers of the scientific and professional conference on natural resources and environmental protection "Ecological Truth" (2003-2009)*

ORGANIZER	***SCIENTIFIC AND PROFESSIONAL CONFERENCE ON NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION "ECOLOGICAL TRUTH"***						
	XI	***XII***	***XIII***	***XIV***	***XV***	***XVI***	***XVII***
	EkoIst'03	***EkoIst'04***	***EkoIst'05***	***EkoIst'06***	***EkoIst'07***	***EkoIst'08***	***EkoIst'09***
University of Belgrade, Technical Faculty in Bor	X	X	X	X	X	X	X
Institute for Public Health - Zajecar	X	X	X	X	X	X	X
Society of Young Researchers Bor	X	X	X	X	X	X	X
Institute of Mining and Metallurgy - Bor							
Center for Agricultural Research Zajecar	X	X	X	X	X	X	
RTB BOR Group							
Health Center Bor							
Ministry of Environment and Development SRJ							
Ministry of Environmental Protection RS							
Community of Negotin							
Ecological movement "Dubasnica"							
University of Nis, Faculty of Occupational Safety Nis					X	X	

Table 6 *Organizers and co-organizers of the International scientific – professional conference "Ecological Truth" (2010-2017)*

ORGANIZER	***INTERNATIONAL SCIENTIFIC AND PROFESSIONAL CONFERENCE "ECOLOGICAL TRUTH"***							
	XVIII	***XIX***	***XX***	***XXI***	***XXII***	***XXIII***	***XXIV***	***XXV***
	Eco-Ist'10	***Eco-Ist'11***	***Eco-Ist'12***	***Eco-Ist'13***	***Eco-Ist'14***	***Eco-Ist'15***	***Eco-Ist'16***	***Eco-Ist'17***
University of Belgrade, Technical Faculty in Bor	X	X	X	X	X	X	X	X
Institute for Public Health - Zajecar		X	X					
Society of Young Researchers Bor	X	X	X	X	X	X	X	X
Institute of Mining and Metallurgy - Bor		X	X	X	X			X
Institute for Nature Conservation of Serbia - Belgrade		X	X		X	X	X	X
Bor Administrative District – Bor		X						
Community of Bor		X						
Touristic Organization "Bor" - Bor		X						
Students Alliance Bor - Bor		X	X		X			
West Backa Administrative District - Sombor	X							
Institute for Public Health Sombor	X							
"Vojvodina forests"Property of Sombor	X							
Regional Chamber of Commerce - Novi Sad	X							
Agriculture Professional Service - Sombor	X							
Community of Apatin	X							
Town Sombor	X							
RTB BOR Group				X				
Freeport-McMoRan Copper & Gold Inc.				X				
Rakita Exploration Bor				X				
Geoing Group Beograd				X				
British-Serbian Chamber of Commerce				X				
University of Montenegro, Faculty of Metallurgy and Technology Podgorica, Montenegro					X			
University of Zagreb, Faculty of Metallurgy Sisak, Croatia					X	X	X	X
University Christian "Dimitrie Cantemir", Faculty of Management in Tourism and Commerce Timisoara, Romania					X	X	X	X
University in Banja Luka, Faculty of Technology, Banja Luka, RS, B&H							X	
University of Pristina, Faculty of Technical Science, Kosovska Mitrovica, Serbia						X	X	X

Table 7 *Venue and the Presidents of the Scientific and Organizing committees*

Conference	Venue	President of the Scientific Committee	President of the Organizing Committee
I	Zajecar		Petar Paunovic
II	Borsko jezero	Dr Rade Kojdic	Toplica Marjanovic
III	Borsko jezero	Dr Petar Paunovic	Zvonimir Milijic
IV	Kladovo	Prof. dr Nedeljko Magdalinovic	Ljubiša Đorđevic
V	Donji Milanovac	Prof. dr Berislav Ristic	Toplica Marjanovic
VI	Negotin	Prof. dr Stevan Stankovic	Srđan Markovic
VII	Zajecar	Prof. dr Stevan Stankovic	Dušan Pejcic
VIII	Soko Banja	Prof. dr Stevan Stankovic	Nadežda Nikolic
IX	Donji Milanovac	Prof. dr Zvonimir Stankovic	Predrag Marušic
X	Donji Milanovac	Prof. dr Stevan Stankovic	Predrag Marušic
XI	Donji Milanovac	Prof. dr Stevan Stankovic	Doc. dr Radoje Pantovic
XII	Borsko jezero	Prof. dr Stevan Stankovic	Prof. dr Zoran Markovic
XIII	Borsko jezero	Prof. dr Stevan Stankovic	Prof. dr Zoran Markovic
XIV	Soko Banja	Prof. dr Stevan Stankovic	Prof. dr Milan Trumic
XV	Soko Banja	Prof. dr Stevan Stankovic	Prof. dr Milan Trumic
XVI	Soko Banja	Prof. dr Stevan Stankovic	Prof. dr Milan Trumic
XVII	Kladovo	Prof. dr Stevan Stankovic	Prof. dr Zvonimir Stankovic
XVIII	Banja Junakovic, Apatin	Prof. dr Zoran Markovic	Prof. dr Zoran Markovic
XIX	Bor	Prof. dr Zoran Markovic	Prof. dr Zoran Markovic
XX	Zajecar	Prof. dr Milan Antonijevic	Prof. dr Zoran Markovic
XXI	Borsko jezero	Prof. dr Radoje Pantovic	Prof. dr Radoje Pantovic
XXII	Borsko jezero	Prof. dr Milan Antonijevic	Prof. dr Radoje Pantovic
XXIII	Kopaonik	Prof. dr Milan Antonijevic	Prof. dr Radoje Pantovic
XXIV	Vrnjacka Banja	Prof. dr Dragana Zivkovic	Prof. dr Radoje Pantovic
XXV	Vrnjacka Banja	Prof. dr Zoran Markovic	Prof. dr Radoje Pantovic

Table 8 *Number of authors and publications of papers*

Conference	Number of authors and co-authors	Publication of papers		
		Publication	Number of pages	Format
I	20	Journal "Razvitak"	20	
II	410	Proceedings	300	B5
III	260	Proceedings	678	B5
IV	250	Proceedings	510	B5
V	230	Proceedings	572	B5
VI	200	Proceedings	492	B5
VII	100	Proceedings	346	B5
VIII	260	Proceedings	728+216	B5
IX	240	Proceedings	680	A4
X	300	Proceedings	662	A4
XI	314	Proceedings	560	A4
XII	291	Proceedings	672	B5
XIII	261	Proceedings	718	B5
XIV	210	Proceedings	619	B5
XV	267	Proceedings	746	B5
XVI	272	Proceedings	664	B5
XVII	252	Proceedings	452	B5
XVIII	213	Proceedings	539	B5
XIX	240	Proceedings	687	B5
XX	245	Proceedings	649	B5
XXI	301	Proceedings	717	B5
XXII	267	Proceedings	649	B5
XXIII	356	Proceedings	797	B5
XXIV	386	Proceedings	882	B5
XXV	278	Proceedings	682	B5
$\sum$	**6423**	**-**	**15237**	**-**

During the previous period, in these twenty-five scientific-professional meetings, including the Day of Preventive Medicine, 2915 papers were published in 30 different sections. In the section "Scientific Youth" 168 papers were published, which makes a total of 3083 papers. Also, twenty-five Proceedings (22 formats B5 and 3 A4 formats) were printed on a total of 15237 pages. The conference was attended by over 6423 authors and co-authors of papers and a large number of invitees, guests, journalists and interested individuals.

"Ecological Truth" was organized in 7 cities of Timocka krajina and 3 cities outside Timocka Krajina. The Organization was led by 12 Presidents of the Organizing Committee, while 10 prominent scientists chaired the Scientific Commmittees that took care about scientific and technical values of the Conference.

INSTEAD OF THE CONCLUSION

"Ecological Truth" is the only conference in this region, and wider, which has gathered all generations for the last twenty-five years, from pupils and students to professors and foreign research workers.

A large number of experts contributed to the success of the "Ecological Truth" from the Institute and from many other institutes and faculties, the Institute for Health Care in Serbia and other organizations, such as the "Society of Young Researches".

The Society of Young Researchers Bor has been one of the permanent co-organizers of the scientific-orifessional meeting "Ecological Truth" since the first conference in 1993. Since then, the co-organizers have been changed and among the large number of new co-organizers, the Society of Young Researchers Bor is the only traditional co-organizer.

A special contribution was made by the Military Medical Academy in Belgrade with its professors Mirce Obradovic and Spiro Radulovic, prof. Stevan Stankovic from the Faculty of Geography as a long-time president of the Scientific Committee, late prof. Zoran S. Markovic from the Technical Faculty in Bor and others.

In addition to scientific-professional work, special attention was paid to accompanying activities. The goal of numerous excursions was to get acquainted with the culture and natural heritage of eastern Serbia, and later Apatin, Kopaonik, Goc and Vrnjacka Banja. Participants of the event had the opportunity to get to know the beauties of the Lazarev canyon and the Zlotska cave, the Djerdap Gorge, the Bor Lake, the Moravica canyon and the thermo-mineral springs Sokobanja. Travelling by boat, they met the values of the Danube and cultural treasures of Kladovo, Apatin. They visited the first urban settlement in Europe, "Lepenski Vir", visited Rajacke pimnice, Sokograd, Jama, Vidikovac, RTB Bor, then museums in Negotin and Zajecar, the birthplace of Stevan Mokranjac and many other cultural sights.

Finally, we can say that "(Our) Ecological Truth" has great strength. Its strength is reflected in its successful living and being held every year in the 21^{st} century.

ACKNOWLEDGEMENT

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HYBRID CELLULOSE BASED ADSORBENTS APPLICABLE IN THE REMOVAL OF HEAVY METALS FROM WATER

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Abstract

The impressive mechanical properties of nanocellulose give it considerable potential to improve the structural and the functional properties of polymer composites. The reinforcing capabilities of cellulose nanoparticles lie also in their structural surface characteristics. This study focuses on the application of the properties of the modified cellulose nanoparticles composites for water purification. Heavy metals such as arsenic and cadmium are among the water pollutants most harmful to human health and the nanocellulose based adsorbents have found their successful use in removing them from water. Therefore, two efficient adsorbent types, based on nanocellulose, are presented in this study.

Keywords: Heavy metals, Water treatment, Nanocellulose

INTRODUCTION

Materials represent one of the most prominent industries in the today's world. Nanotechnology is recognized as one of the most successful areas for technological development. Due to the progress of nanotechnology and the recent rising concerns about environmental issues, there is an increasing demand for the products made from renewable and sustainable non-petroleum based resources. Considering this, natural fibers have been considered more and more of interest because of their promising characteristics, such as biodegradability, renewability and low price. Among these natural fibers, cellulose as the biopolymer which exists in a wide variety of living species including plants, bacteria and even some animal species, has been the subject of the extensive research in nanotechnology. Functional nanomaterials are especially attractive because they enable the production of materials with improved various special properties, possessing potential applications in various fields [1].

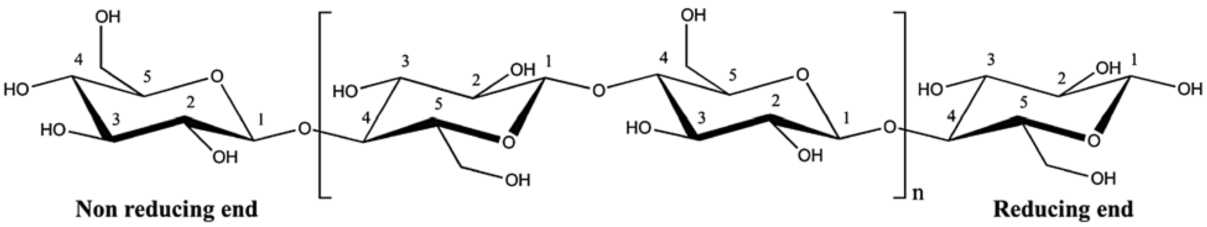

Figure 1 *Chemical structure of cellulose*

Because of their nanoscale dimensions, the cellulose nanoparticles display a high surface area and their surface hydroxyl groups enable targeted surface modification which is performed to introduce some desired surface functionality [2]. However, the surface physico-chemical properties of cellulose nanoparticles is primary governed by the extraction procedure used to prepare these nanoparticles from the native cellulosic substrate [3]. Figure 2 shows the surface functionalization provided by the most common extraction methods.

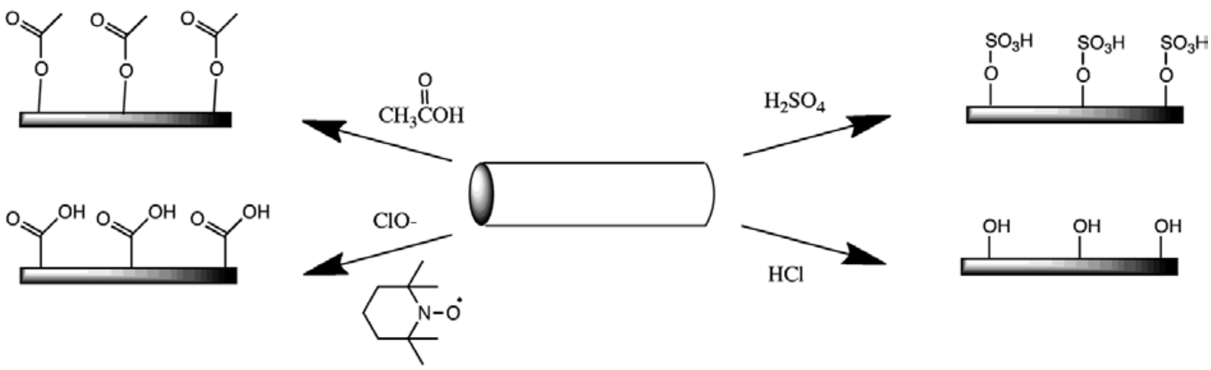

Figure 2 *Common syntheses of nanocellulose provide for distinctive surface chemistries*

Different chemical modifications of nanocellulose can be divided roughly into three major groups: the preparation of negatively charged, positively charged, and hydrophobic nanocellulose [1,4,5]. This review deals with the application of various forms of nanocellulose for the environment protection, specifically water purification.

Considering the water pollution by heavy metals, arsenic (As) and cadmium (Cd) are among those which the World Health Organization designated as particularly harmful to human health. According to the recommendations of the World Health Organization the highest permissible concentrations of heavy metals like arsenic, cadmium and lead in drinking water are limited to 0.01 mg L^{-1} for arsenic and 0.003 mg L^{-1} for cadmium. Low restrictive boundaries for these heavy metals have imposed a challenging problem in the control of environmental pollution. A wide range of water treatment technologies such as chemical precipitation, ion exchange, membrane filtration, and adsorption may be used for the removal of heavy metals, but these methods of water treatment still suffer from certain limitations, economical, or technological. Adsorption turned out to be one of the most rewarding and the most commonly used methods in the study of new materials and the conditions for the removal of heavy metals from water [6-12].

The development and the application of new nanostructured materials in the field of water treatment has enabled the development of their various combinations of modification and functionalization in order to synthesize a high-capacity adsorbents with the possibility of multiple applications, minimal environmental impact and also to make them profitable regarding their possible use [11,12].

Here is presented a part of a study on the magnetite (MG), rock mineral and one of the main iron ores, based high performance adsorbent, with nanocellulose (NC) support, for the arsenic (As^{5+}) removal (NC-MA/L-MG) [13].

Besides that, in this review is presented a part of the research on a novel adsorbent, NC-PEG [14]. It is obtained by the modification of NC with PEG-6-arm amino polyethylene glycol ($PEG-NH_2$) *via* maleic anhydride (MA) linker, and was tested for the removal of Cd^{2+} and also Ni^{2+}, which is also considered a harmful heavy metal, from water with successful results. A subsequent precipitation of iron oxide (FO) from goethite on NC-PEG was employed to produce NC-PEG/FO adsorbent which was used for As^{5+} and As^{3+} removal.

MATERIALS AND METHODS

NC-MA/L-MG [13]

All the chemicals used in this study were of analytical grade and used as received. The preparation of adsorbents was performed through the five consecutive steps, applying the magnetic stirrer (*Heidolph*) and the ultrasonic treatment (*Bandello electronic*, *Berlin*, *Germany*, *power 120 W*, *frequency 35 kHz*), or the combination of both methods. The ultrasound assisted synthesis enhanced the reaction efficiency of some reaction steps [15,16]. NC was produced from the cotton microfibers by treating with sulphuric acid. The product was diluted with distilled water (DW), neutralized to pH 6, and three cycles of centrifugation/DW water washing were applied. After that, NC was filtered using polytetrafluoroethylene filter membrane. Then it was modified by maleic anhydride (MA) and subsequently with ethylenediamine (EDA), denoted as NC-MA/EDA. Then, the tetraethyl ester of ethylenediaminetetraacetic acid (EDTA) was added. The reaction took place under the ultrasonic treatment and then it was followed by the magnetic stirring at room temperature. The product was washed with ethanol, vacuum dried and denoted as NC-MA/EDA-EDTA. Then the product was subjected to the ultrasound treatment in *N,N*-dimethylformamide (DMF) for 5 min, with drop-wise addition of EDA followed by the heating/mixing at magnetic stirrer. The obtained product was washed by using abundant quantity of DMF and DW, dried under vacuum, and denoted as NC-MA/EDA-EDTA-EDA (NC-MA/L). It was then dispersed in $FeSO_4 \cdot 7H_2O$ of different concentration and homogenization was performed by the ultrasonic treatment under the inert atmosphere. The Response Surface Methodology (RSM) was applied for the optimization of the step of MG precipitation in order to obtain the uniform and the attrition resistant precipitate of MG. After sonication the NC dispersion was transferred to the oil bath, with constant gentle mixing, and the temperature was adjusted using the magnetic stirrer/heater. An oxygen-free solution contained different quantity of reactants, KNO_3 and KOH was added for 30 min providing the continuous iron oxide precipitation. After the precipitation, the reaction mixture was heated, and left overnight. The adsorbent NC-MA/L-MG was isolated in the form of the precipitate and washed with DW until getting free from ions in filtrate.

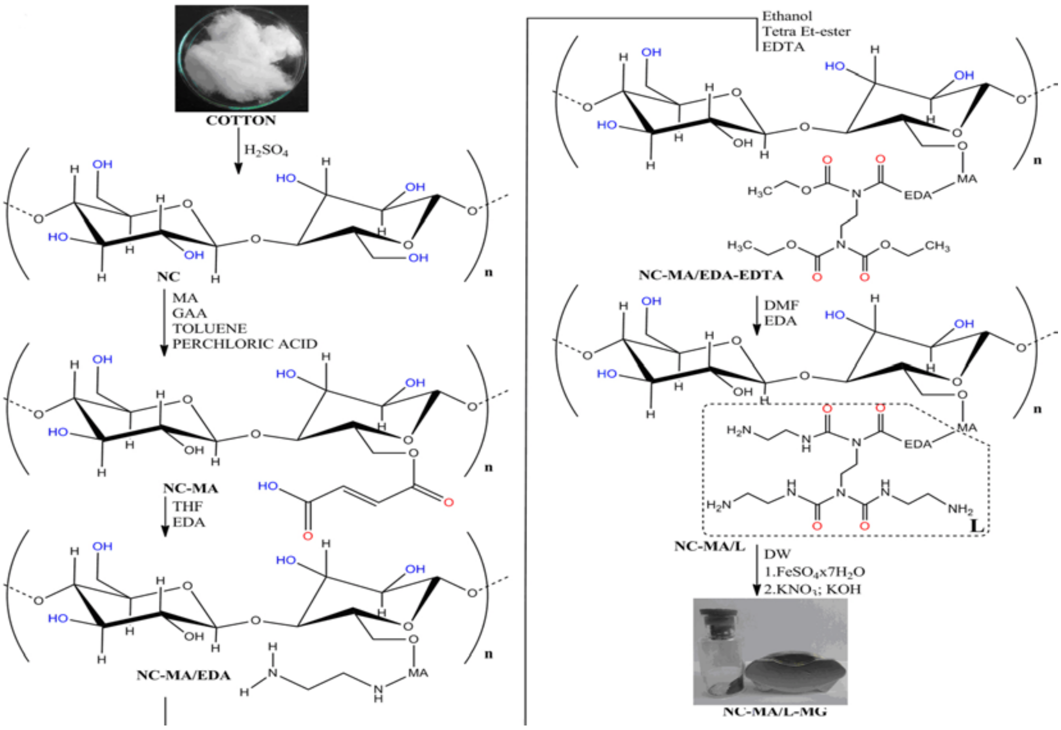

Figure 3 *The modification paths applied for NC-MA/L-MG*

NC-PEG [14]

The nanocellulose (NC) isolation [17] and afterwards the subsequent modification with maleic anhydride (MA) [18] to produce NC-MA, and NC-MA modification with PEG-6-arm amino polyethylene glycol ($PEG-NH_2$) to prepare NC-PEG adsorbent, was carried out.

NC-PEG was sonicated in deionised (DI) water with the simultaneous introduction of N_2. The reaction was conducted continuously, under magnetic stirring and in inert atmosphere, by the drop-wise addition of $FeSO_4 \cdot 7H_2O$ solution with concentration. The ferri/ferro oxidation was performed by changing the nitrogen with air introduction and neutralizing the reaction mixture, which caused the precipitation of iron oxide into the goethite (iron bearing hydroxide mineral) ore [19]. The reaction was conducted until the green-blue colour of the solution changed to ochre shade. The obtained product was filtered, washed with DI water, and the freeze-drying was conducted by cooling and keeping the freshly obtained material. The procedure for the precipitation of iron oxide (FO) was repeated in an analogous manner, and the obtained adsorbent was named NC-PEG/FO.

RESULTS AND DISCUSSION

NC-MA/L-MG [13]

The multi-step synthesis of the adsorbent was applied in order to design the material with the appropriate geometry, surface properties and pore structure. The textural properties and zero point of charge (pH_{PZC}), before and after adsorption, are summarized in Table 1.

***Table 1** Textural properties and pH_{PZC} of NC-MA/L-MG adsorbent*

Adsorbent	Specific surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)	pH_{PZC}[a]	pH_{PZC}[b]
NC-MA/L-MG	85.30	0.71	15.20	6.50	5.70

[a] Before and [b] after adsorption; pH_{PZC} of NC was found to be <1, and pH_{PZC} of NC-MA <3.

The high values of the specific surface area and the pore volume are properties in favour of NC-MA/L-MG. The literature data on the unmodified nanofibrillated cellulose [20], showed that the differences in the surface area and pore diameter are generally influenced by the textural properties of a substrate and of the applied modification method, as well as the post processing of obtained material. In contrast to the applied mild thermal treatment for NC-MA/L-MG production, the high temperature processing exerts significant change in textural properties of final material. The precipitation of MG on NC-MA/L provided the conditions applicable for the preservation of organic branched structures with the controllable deposition of the nanoscale materials. The shift of pH_{PZC} value (Table 1) indicates the specific arsenate adsorption, rather than the electrostatic interaction, and the formation of the complexed/precipitated arsenic species at surface of the magnetite based adsorbent is a main adsorption mechanism [15,16].

The morphology of NC-MA/L (Figure 4a) indicated the surface coverage by the organic material due to the chemical modification, and the subsequent MG deposition affects the morphological structure of the surface of NC-MA/L-MG (Figure 4b).

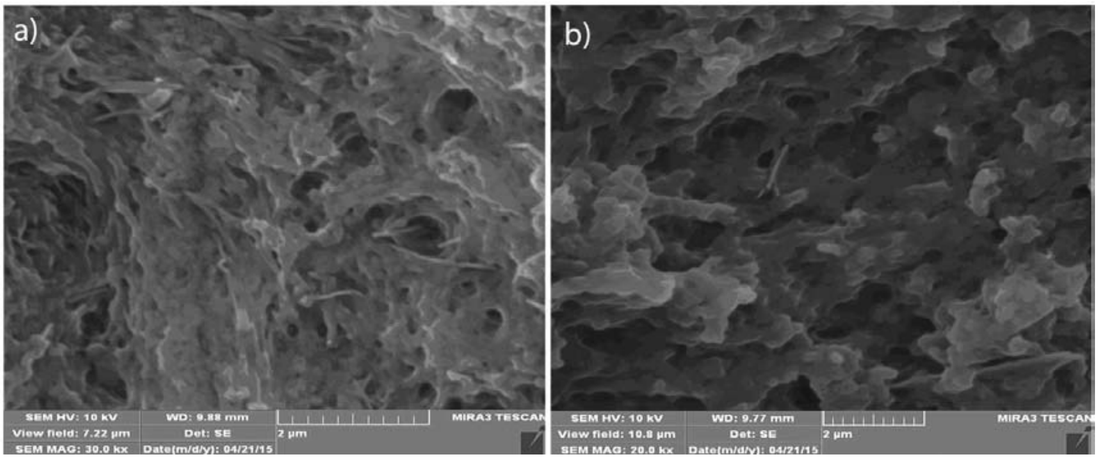

***Figure 4** SEM images of NC-MA/L (a) and NC-MA/L-MG (b)*

Considering the significance of the influence of pH on the arsenic speciation and the ionization state of the adsorbent surface, it was important to study the influence of pH on the effectiveness of As removal. The results of the pH-dependent adsorption study, *i.e.* As removal *versus* the initial pH (pH_i) for the NC-MA/L-MG adsorbent, and the change of the final pH (pH_f) in relation to the initial pH (pH_i) are shown in Figure 5. The extent of the adsorption pH_f/pH_i relation is affected by both release/consumption of the hydrogen ions, protonation/deprotonation of MG surface, and the pH-dependent arsenic speciation.

Both the surface state and the As^{5+} speciation plays the significant contribution to the electrostatic interactions between surface/ions causing intensity of As flux toward the specific adsorption sites at $pH_i > pH_{PZC}$. The deprotonation of the surface functional groups increased the concentration of the negatively charged arsenic species and the competition of the hydroxyl ion, so that lower adsorption efficiency is a consequence.

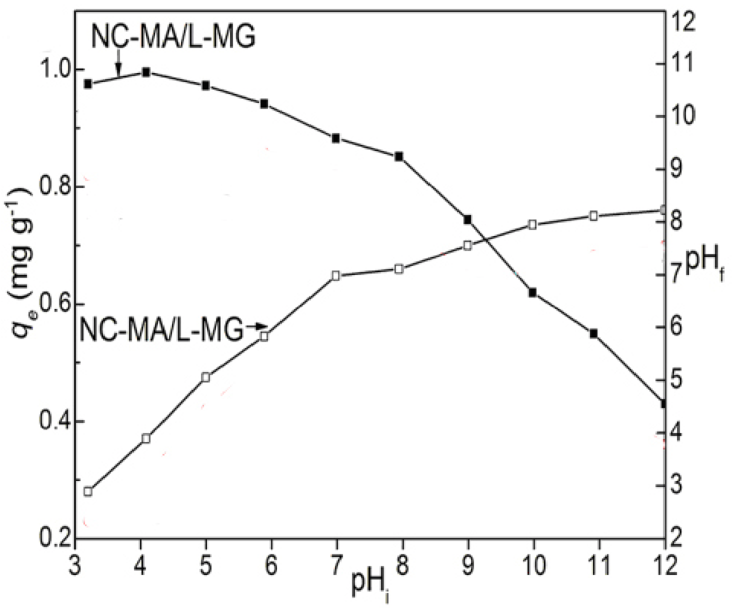

Figure 5 *Effect of pH on the adsorption of As^{5+} on NC-MA/L-MG*

NC-PEG [14]

The multi-step adsorbent synthesis was performed in order to produce the adsorbent materials, namely NC-PEG and NC-PEG/FO with the appropriate geometry, morphology and porosity. The determined values of the textural properties and point of zero charge values (pH_{PZC}) - the condition when the electrical charge density on a surface is zero, are summarized in Table 2.

Table 2 *Textural properties and pH_{PZC} of the studied adsorbents*

Adsorbent	Specific surface area, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$	Pore diameter, nm	pH_{PZC}^{a}	pH_{PZC}^{b}
NC-PEG	38.7	0.72	17.4	6.9	6.4
NC-PEG/FO	62.1	0.80	26.4	8.5	7.6

[a] Before and [b] after adsorption; pH_{PZC} of NC < 1, and pH_{PZC} of NC-MA < 3.

It was found that the cations were strongly bonded to amino groups, by the complexation/chelation interactions, and the higher nucleophilicity of the amino groups, at pH higher than pH_{PZC}, led to stronger interaction with Cd^{2+} and Ni^{2+} cations.

Due to the different properties of NC and the synthesized materials, higher values of the specific surface area were obtained for both NC-PEG and NC-PEG/FO than for NC. Additionally, the shift of the pH_{PZC} value indicated the specific arsenate adsorption rather than the electrostatic interaction, as well as the formation of the complexed/precipitated arsenic species, at the surface of the goethite based adsorbent. The determination of the iron content in the acidic extract, obtained using 10% nitric acid and microwave digestion, showed that 11.7% of the iron was precipitated in goethite form at the NC-PEG surface.

The morphology of NC-PEG and NC-PEG/FO indicated the surface coverage by the organic material. The chemical treatment followed by FO deposition affected the morphological structure of the surface of NC-PEG/FO (Figure 6). The evolution of the NC-PEG/FO morphology could be explained by the heterogeneous reaction between FO and the terminal amino-branched structures at the NC-PEG grains.

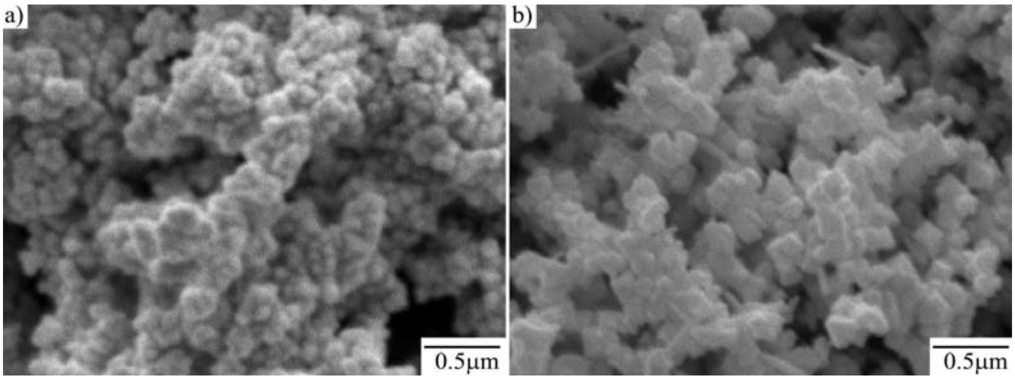

Figure 6 *SEM images of NC-PEG (a) and NC-PEG/FO (b)*

As it is known that the pH influences the equilibrium of ionic species and protonation/deprotonation of the sorbent functional groups, the degree of As^{5+}, As^{3+}, Cd^{2+} and Ni^{2+} removal *vs.* initial pH (pH_i), in the presence of the studied adsorbents, are presented in Figure 7.

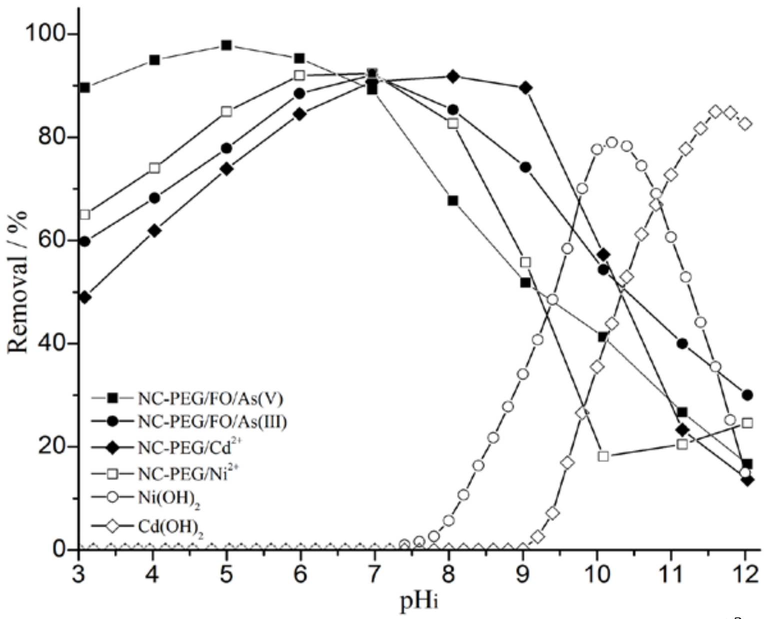

Figure 7 *Effect of pH on As(V) and As(III) removal by NC-PEG/FO, and Cd^{+2} and Ni^{2+} removal by NC-PEG*

From Figure 7 it can be noticed that the gradual decrease of the percentage of As^{5+} and As^{3+} adsorption on NC-PEG/FO started at pH > 7. According to the pH-dependent ionization of $As^{5+}$and As^{3+}, the highest adsorption capacity showed the most effective removal at pH in the vicinity of p*K*a. The charged As species participated in different electrostatic interactions (attraction/repulsion) with the surface/ions charges, thus influencing the intensity of the As flux toward the specific adsorption sites. The positively charged surface of NC-PEG/FO adsorbent at pH < pH_{PZC}, attracted the negatively charged arsenate, causing higher intensity of the As flux toward the adsorbent surface. The opposite was valid at higher pH. The selection of the optimal pH 6 was dictated by the following factors: the adsorption capacity, the adsorbent deposit stability (dissolution) and the consideration of the techno-economic indicator.

CONCLUSION

The novel designed NC-MG based adsorbent (NC-MA/L-MG) with the organic support and with the inorganic precipitated adsorptive material (MG) displayed rather favourable adsorption properties toward As^{5+}. The morphological/textural characteristics of the presented adsorbent caused its significant adsorptive properties and it is therefore recommended for further application.

Furthermore, the adsorption performance of NC-PEG and NC-PEG/FO was analysed as a consequence of the adsorbent specific surface area, as well as of their hybrid nature. The experimental results showed that the used adsorbents were also efficient and reusable for cations and As^{5+} removal from natural water. The advantage of a novel environmentally friendly adsorbent material NC-PEG, obtained by the multistep adsorbent synthesis, is that it could be used as the high performance adsorbent for Cd^{2+} and Ni^{2+} removal. Also, an additional modification of the NC-PEG adsorbent, by the goethite precipitation, produced NC-PEG/FO adsorbent applicable for As^{5+} and As^{3+} removal.

Generally, both adsorbent types are useful and efficient for water purification, however, as the results display, NC-PEG and NC-PEG/FO have a possibility for wider application.

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Conference Papers

MONTE CARLO SIMULATION FOR THE EVALUATION OF MEASUREMENT UNCERTAINTY OF PHENOLIC COMPOUNDS IN CONCRETE

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Abstract

Phenolic compounds from building materials negatively affected overall quality of people's life. This study present two approaches for evaluated uncertainty results measurements of phenolic compounds in concrete: GUM recommendations and Monte-Carlo simulated method. Disagreement in those methods was achieved. Monte-Carlo simulated method could be used in evaluation of combined measurement uncertainty for phenolic compounds analysis in concrete.

Keywords: Uncertainty, GUM, Monte Carlo

INTRODUCTION

Guide to Expression of Uncertainty in Measurement (GUM) embraces many aspects of uncertainty evaluation. Therefore, it was widely used, respected and recognized by many as the master document on uncertainty. In this research some deficiencies and limitations were noticed. In order to revise and promote the use of GUM and the International Vocabulary of Basic and General Terms in Metrology (VIM), and prepare supplemental guides for GUM, [1] the international organizations that prepared the original version of GUM, formed the Joint Committee for Guides in Metrology (JCGM).

The basic document in the JCGM 100 series [2] is based on the law of propagation of uncertainty (LPU). LPU [3] can be used under following conditions: only one output quantity appears in the model, the model is explicit, i.e. it can be written as $c = f(X1,\ldots,XN)$ (although the function c does not need to be analytic), and the model is well approximated by its linear expansion around the best estimates of the input quantities.

After obtaining the standard uncertainty by using the LPU, GUM approach uses the Welch-Satterthwaite formula to obtain the effective degrees of freedom, necessary to calculate the expanded uncertainty. Since the analytical evaluation of the effective degrees of freedom is still an unsolved problem, the GUM is not always appropriate. Moreover, GUM assumes the validity of the central limit theorem, i.e. it assumes that the probability density function (PDF) of the output is approximately normal and can be represented by a student t-distribution. In some cases, this resulting distribution may have an asymmetric behavior or tend to a normal distribution, which implies less validity of GUM [4]. One way to overcome these constraints is to use methods that contain a more information for estimation of measurement uncertainty than GUM. This work presents a methodology that uses Monte Carlo method for propagation of distributions, which is described in JCGM 101 [5]. A difference between two approaches is illustrated by Figures 1a and 1b which presents propagation of uncertainties and propagation of distributions, respectively. In case of distributions propagation, a complete information of the input quantities is available, while in the case of propagation of uncertainties, an input consists only of expectation and standard deviation of input quantities (only the first and the second central moments).

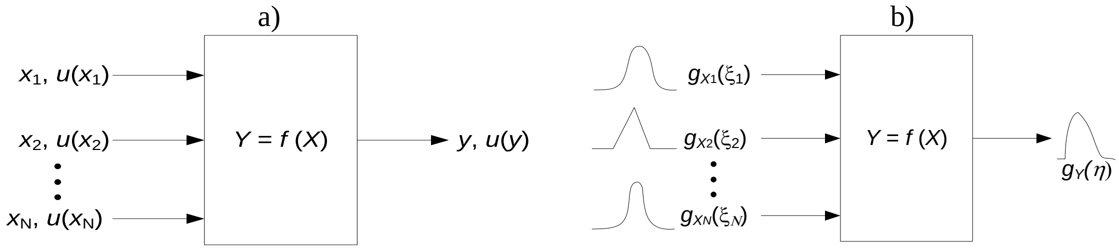

***Figure 1** (a) Propagation of uncertainties, where $x_1, x_2, \ldots, x_N$ are input quantities and $u(x_1), u(x_2), \ldots, u(x_N)$ are their uncertainties; y and u(y) are measurand and its uncertainty. (b) Propagation of distributions, where $g_{X1}(\xi_1)$, $g_{X2}(\xi_2), \ldots, g_{XN}(\xi_N)$ are distribution functions of the input quantities and $g_Y(\eta)$ is the distribution function of the mesurand*

The aim of the presented study was a critical assessment of two alternative approaches approved nowadays for estimation of combined uncertainty of measurement. Both the Guide to Expression of Uncertainty in Measurement (GUM) recommendations and Monte-Carlo simulated method were used for estimation of uncertainty associated with analysis of phenolic compounds in concrete.

MATERIALS AND METHODS

Uncertainty estimation

Monte Carlo approach for evaluation of uncertainty is a reliable tool when GUM framework is not adequate [6]. Therefore, besides analysis of measurement uncertainty by GUM method, the Monte Carlo method used for estimation of measurement uncertainty in C++ programming language is implemented. A procedure for application of Monte Carlo method was performed in the following way:

- The number of histories M in MC simulation was selected.

- N input values and estimate their distribution functions were defined.

- M vectors were generated, by sampling from the PDFs assigned to input quantities Xi, i=1…N.

- For each vector, the corresponding model Y was created.

- Obtained values of models were sorted into increasing order.

- The output value was estimated and uncertainty was measured.

- For chosen coverage probability p, an appropriate coverage interval was formed (in case of asymmetric PDF it is the shortest 100p percentage coverage interval).

RESULTS AND DISCUSSION

The content of phenol in a concrete sample was determined according to equation (1):

$$c = \frac{y-a}{b}\frac{V}{m}\frac{100}{R} \qquad (1)$$

where y is the peak area of phenol compound, a and b are the slope and the intercept of straight-line fit to a data set, obtained by an application of the method of least squares, V is the volume of solution, m is the mass of sample and R is recovery.

In accordance with the GUM [1,2], all potential sources of the measurement uncertainty have been considered. Also, the contribution to uncertainty of measurements was estimated in a way that uses all available information about the measurement procedure considering that during propagation of uncertainty and propagation of distribution was not transmit more information than that which is known. In order to identify all relevant uncertainty sources, a cause-effect diagram is drafted (Figure 2). All needed information about uncertainty is summarized in Table 1.

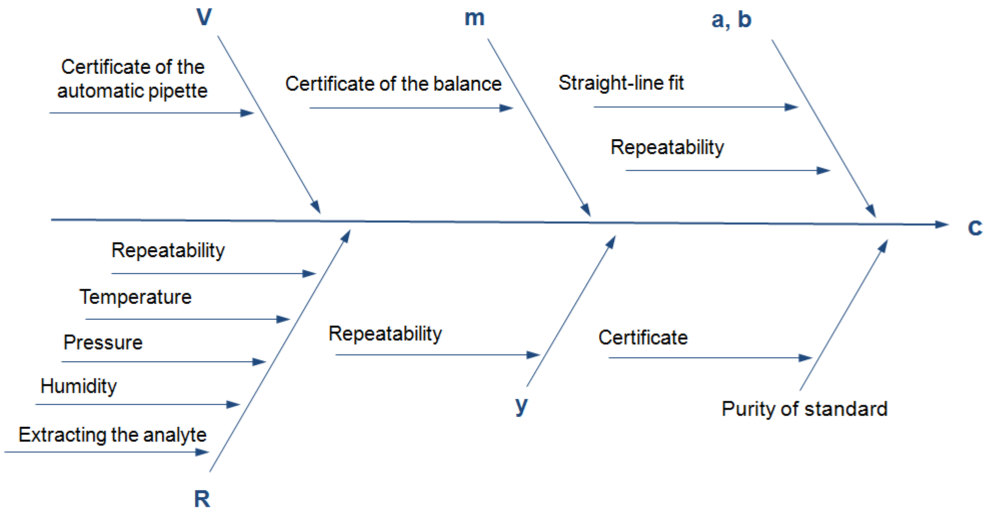

Figure 2 *Cause-effect diagram*

Table 1 *Uncertainty sources and associated distributions with their respective parameters for the estimation of uncertainty*

Uncertainty source	Distribution	Parameters of a distribution
Volume (V)	Normal	Mean: 75 ml; SD: 2.55 ml
Mass (m)	Normal	Mean: 10 g; SD: 0.22g
Recovery (R)	Student's t Location-Scale	Mean: 78.80 %; SD: 3.93 %; DF: 3
The area of peak (y)	Student's t Location-Scale	Mean: 194071; SD: 9500; DF: 3
Slope (a)	Student's t Location-Scale	Mean: 20055; SD: 2912; DF: 3

*SD – Standard Deviation; DF – Degrees of Freedom

The results obtained by processing the set of available information by GUM uncertainty approach and corresponding statistical parameters obtained by Monte Carlo simulation are illustrated in Table 2. Deviation of PDF of the output estimated by Monte Carlo simulation from distribution assigned to measurand through GUM analysis is shown in Figure 3. It can be seen that these two ways of expressing measurement results are in disagreement. Since these disagreements come from the assumptions and approximation included in GUM Uncertainty Framework, for analysis of this kind of uncertainty the Monte Carlo method described in JCGM 101:2008 is proposed.

***Table 2** Results obtained using the GUM and Monte Carlo uncertainty approach for uncertainty estimation*

Parameter (GUM)	Value (mg/kg)	Parameter (MC)	Value (mg/kg)
Mean	3.56	Mean	3.56
Combined standard uncertainty	0.32	*Low endpoint for 95%	2.66
Expanded uncertainty for 95%	0.71	*High endpoint for 95%	4.59
Parameter (GUM)	Value (mg/kg)	Parameter (MC)	Value (mg/kg)

*These values are the limits of the shortest 95% coverage interval

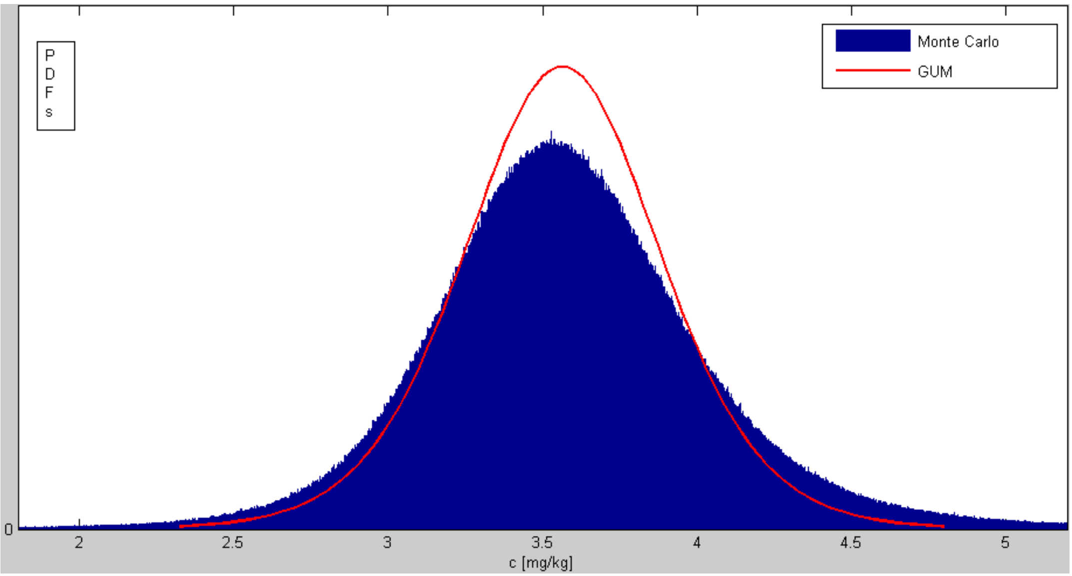

***Figure 3** Comparison of PDFs obtained with GUM and Monte Carlo method*

CONCLUSION

This study was shown that there is disagreement in the estimation of combined uncertainty of measurement using GUM recommendations and Monte-Carlo simulated method. Monte-Carlo simulation is proposed as better method in estimation of measurement uncertainty for analysis of phenolic compounds in concrete.

ACKNOWLEDGEMENT

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AGGREGATION AND HUMIFICATION DEGREE OF HUMIC ACIDS FROM TECHNOSOLS ON RECLAIMED Cu POST-FLOTATION TAILINGS (BOR, SERBIA)

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Abstract

Part of Cu post flotation tailings of Copper Mine Bor were reclaimed by reconstructing the topsoil with arable soils and revegetation in 1991. Humic acids were isolated from these Technosols and their aggregation, strongly influencing metal binding in soil, was investigated. Six humic acids were isolated from Technosols differing in pH, organic C and clay content. Two groups of humic acid control samples were chosen: the first from arable soils originating from the vicinity of Bor, which surface soil layers were used for reclamation, and the second from soils formed under different environmental conditions. Optical properties, aggregate particle size and zeta potential were determined by UV-VIS, ATR-FTIR and Dynamic Light Scattering. According to UV-VIS results, humic acids belong to the type B pointing out to its lower humification degree. Bacis units at pH10 are in the 11.7-26.8 nm range. Pronounced reaggregation (1462-5218 nm) at pH3 points out to less expressed humic acid sol stability, as well as to increase in aromatic condensation degree. Correlation between particle size and E_4/E_6 index at pH10 indicates clear difference between Technosol humic acids and all control samples due to significantly lower degree of aromatic condensation. Under acidic conditions pronounced aggregation and increase in aromatic condensation of Technosol humic acids are obvious. Results obtained have shown changes in Technosol humic acid structure and properties with pH, which likely affect their interaction with metals. The present study precedes future investigations of humic acid binding to metals present at high concentrations in these Technosols.

Keywords: Technosol humic acid, Aggregation, Humification degree

INTRODUCTION

Copper mining and processing have a profound impact on the environment. The consequence is a huge amount of flotation tailings comprising even 96% of the mass of run-of-mine ores with worldwide production estimated to be two billion tons in 2011 [1,2]. One of the largest mines in Serbia is the Copper Mining and Smelting Combine Bor. Beside other mine wastes, post-flotation tailings (PFT) dumps as a result of copper ore processing were formed. The PFT dump "Polje 2" was definitively abandoned in 1987. In addition to degradation of large land areas, these mine wastes are sources of pollution to the surrounding environment. In order to restore the function of a portion of PFT dumps, reclamation measures were implemented. In 1991, an area of about 16 ha was reclaimed by reconstructing the topsoil with natural arable soil, an average depth of 40 cm. The soil was taken from the southern part of the town of Bor where the residential area expanded. One part of the reclaimed area was planted with grass and the other with trees. Previous investigations of reclaimed PFT 20 years after remediation [3] have shown that A horizon (about 45 cm deep) was formed on the soil surface by reclamation process, mixing of natural arable soils with tailings. Most of these soils are characterized by degraded structure, low humus content, predominantly low pH, high As and Cu concentrations, and low soil microbial activity. According to WRB 2007 [4], these soils are classified as RSG Technosols.

Humic substances (HSs) are the most important organic components present in water, soil, and sediments and have significant environmental functions. They are recognized for their role in controlling both the fate of environmental pollutants and the biogeochemistry of organic C in the global ecosystem [5]. Humic substances affect the soil and water properties through their participation in dynamic processes where their constituent molecules interact with other molecules or ions (complexation/decomplexation), solid surfaces (adsorption/desorption), and among themselves (aggregation/deaggregation) [6]. Their roles in removal of heavy metals from soil and water, inhibition of free radicals formation by metal catalysis, reduction, and stabilization of metal nanoparticles are among the most important [7].

Humic substances exhibit different structures under different conditions, i.e., they are able to rearrange and restructure themselves in response to environmental changes such as pH, ionic strength, moisture as well as HS concentration [8-10]. Aggregation properties of HAs significantly influence their interactions in nature, for example metal complexation [11], the reason why it is important to study their colloidal character, i.e., their size and negative surface charge.

Hence, the main goal of this study was to investigate aggregation/reaggregation process of humic acids (HAs) from Technosols on Cu PFT about 20 years after reclamation. Particle size distribution (PSD) and zeta potential (ZP) were measured in highly alkaline solutions (pH10), low HA concentration and low salt concentration/constant ionic strength to obtain HA basic unit size [9]. Alkaline solutions were acidified by HCl to low pH value (pH3) to examine the HA reaggregation ability. Since particle size is closely related to colloidal stability of humic particles [9,12], ZP at both pH values (alkaline and acidic systems) was measured. To relate TC HA agreggation to degree of aromatic condensation, E_4/E_6 index was determined by UV-VIS spectroscopy.

MATERIALS AND METHODS

Soil samples and analyses

Humic acids were isolated from 6 soil samples collected from the A horizon of Technosols on reclaimed Cu PFT "Polje 2", Bor - Serbia (44º05’N, 22º06’E). Five soil samples (TC1-TC5) were taken at a 0-25 cm depth. Sixth soil sample (TC6) was collected at a 15-50 cm depth, from the A horizon covered with a wind-deposited 15 cm thin layer originating from non-reclaimed area of post-flotation tailings. Soil samples were selected due to differences in pH (4.17-7.24), organic C (0.39-1.24%) and clay content (18.46-27.34%). TC1 sample was silt loam, TC2-TC5 were sandy clay loam and TC6 was loam.

To the best of our knowledge, there is no appropriate HA sample which could be used as control (there are no data on TC HA properties immediately after the reclamation as well as of HA properties of arable soils used in the reclamation process). Therefore, two groups of HA control samples were chosen in this study. The first group consisted of three HAs (CB7-9) isolated from natural arable soils (0-25 cm depth) originating from the location nearby a new residential area of Bor, which surface soil layers were used for reclamation of PFT. These control soil samples were selected primarily due to different pHs, namely two were acid (CB7 and CB9) and one alkaline (CB8). The other reason was the mean weight diameter (MWD) of soil aggregates, ranged 1.99-3.65. Control soil samples had significantly higher soil organic C content than Technosols. Their soil texture classes were clay loam and loam. The second group of control samples includes two HAs isolated from soils originating from other locations and formed under different environmental conditions. The first HA (CCH) was isolated from Chernozem (0-25 cm depth), originating from Novi Banovci (44º57'N, 20º16'E), Serbia. Chernozem was alkaline clay loam with 1.89% soil organic C. The second HA control sample (CES) was IHSS standard HA obtained from Elliott Soil [13]. Elliott Soil is silt loam, silty clay loam or loam, moderately acid to neutral [14].

Soil texture, soil aggregate stability to water expressed by the mean weight diameter (MWD), organic C and pH were determined using common methods [15], the soil texture classified according to [16].

Extraction and purification of HA samples

HA sample was isolated using a modified IHSS method (HA gel was dried at 35°C, powdered, and sieved using a 0.05-mm sieve) [17].

Dynamic light scattering (DLS) and laser Doppler electrophoresis (LDE) techniques

To perform PSD and ZP measurements, the HA sols (0.02 gdm^{-3}) were prepared using deionized water and their pHs were adjusted by adding 0.1 and 1.0M HCl or NaOH solutions. NaCl was added to maintain ionic strength constant (0.1 M) within ±10%, even though the maximum amount of HCl or NaOH solution was used. The prepared HA sols were equilibrated for 24 h at (25±2)°C and their pHs determined before the measurement. The measurements were performed using a Zeta-sizer Nano ZS with 633 nm He-Ne laser (Malvern, UK), and data were analyzed by the Zetasizer Software Version 6.20 (Malvern, UK).

PS was determined applying backscatter detection (173° detection optics). Disposable polystyrene size cuvettes (Sarstedt, Germany), filled with 1 mL of sample, were used. Prior to particle size determinations, the instrument was checked by measuring particle-size standards (polystyrene microspheres in water, 60 and 220 nm particle mean diameters, Nanosphere™ Size Standards, Duke Scientific Corporation, USA). For each size standard and HA sol studied, three replicate measurements were performed (3 × 1 mL) and the average size value was calculated. Each measurement consisted of 30 runs and the duration of each run was 10 s. Refractive index value was adopted to be 1.6 [18].

To display size results for highly polydisperse humic solutions, exponential sampling (distribution) method for natural colloidal suspensions [18] was applied. Particle-size distribution (PSD) by intensity was converted to volume distribution and the most intense peak was used as relevant to size determination applying distribution analysis.

The LDE method was applied to measure electrophoretic mobility of HA particles and ZP was calculated according to Henry's equation. ZP measurements were performed in size and ZP folded capillary cells (Malvern, UK). ZP transfer standard (–50 mV, Malvern, UK) was used as a check standard. Three series of five consecutive measurements were performed for each HA and the average ZP value was calculated.

UV-VIS spectroscopy

Absorbances of alkaline and acid sols at 465 and 665 nm were recorded by UV-VIS spectroscopy, Evolution 60s, Thermo Fisher Scientific, USA, to calculate the E_4/E_6 index.

RESULTS AND DISCUSSION

According to UV-VIS results, humic acids belong to the type B pointing out to its lower humification degree. PS versus ZP at pH10 and pH3 are illustrated in Figure 1. It is obvious that ZPs are negative for all HAs at both pHs (-22.7 to -31.9 mV at pH10 and -16.3 to -19.4 mV at pH3). Bacis units of TC HAs at pH10 are in the range 11.7-26.8 nm, except for TC1 (151.4 nm). After acidification, pronounced TC HA reaggregation (1462-5218 nm) is evident, pointing out to less negative ZP values, i.e., less expressed HA sol stability.

a) b)

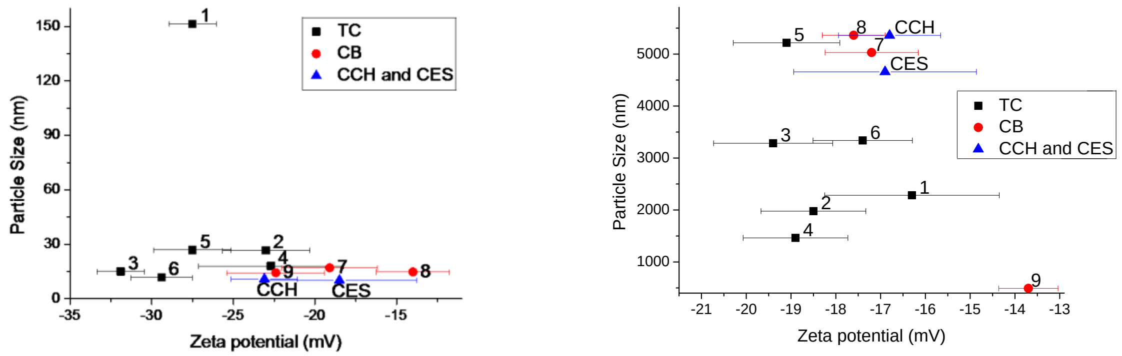

Figure 1 *Relation of particle size and zeta potential at a) pH10 and b) pH3 for humic acids isolated from Technosols (TC1-6) and control natural soils: arable soils near Bor town (CB7-9), Chernozem (CCH) and standard Elliot Soil (CES)*

It is obvious (Figure 1a) that at pH10 all control HAs (CB7-9, CCH and CES) are grouped but not clearly separated from TC HAs. However, all control HAs, except CB9, are grouped and more clearly separated from TC HAs at pH3 (Figure 1b). More pronounced aggregation of CCH and CES HA control samples possibly could be explained by higher relative ATR-FTIR band intensities (data not shown) typical of carboxyl and phenolic (OH) functional groups. On the contrary, aggregation of other samples from the separated group (CB7-8, as well as TC5) could not be explained by already mentioned relative intensities likely due to the presence of two competitive intramolecular contraction and intermolecular aggregation processes influencing HA particle size [8].

Correlation between PS and E_4/E_6 index at pH10 (Figure 2a) indicates clear separation of TC HAs from all control HAs due to significantly lower degree of aromatic condensation (higher E_4/E_6 index values). At pH3 (Figure 3b), where aggregation process is obvious, TC HAs are grouped but not so clearly separated from control HAs. Comparing E_4/E_6 indexes under alkaline and acid conditions, an increase in aromatic condensation degree for TC HAs can be noticed, opposite to its decrease for BC HAs and almost no change for CCH and CES HAs.

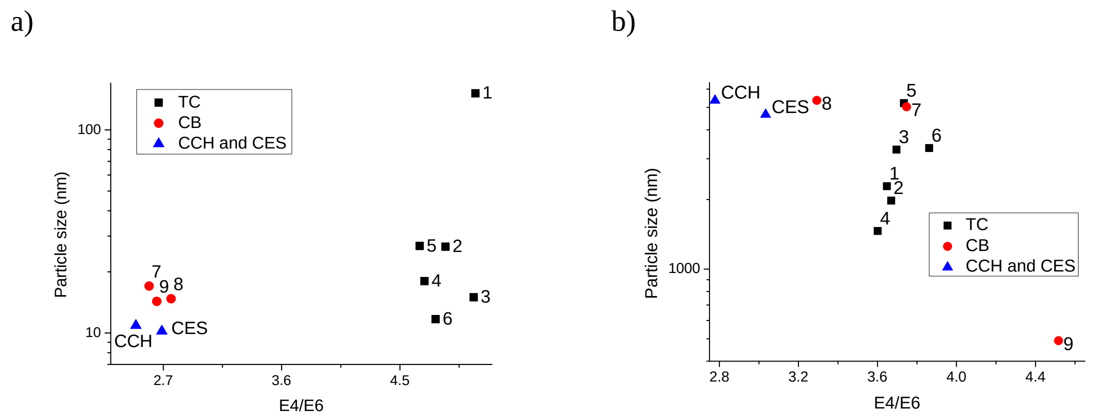

Figure 2 *Relations of particle size and E_4/E_6 at a) pH10 and b) pH3 for humic acids isolated from Technosols (TC1-6) and control natural soils: arable soils near Bor town (CB7-9), Chernozem (CCH) and standard Elliot Soil (CES)*

According to literature [7,19], HA chemical structure and properties significantly influence the efficiency of HA-metal binding. Results obtained in this study have shown changes in TC HA structure and properties with pH, which likely affect their interaction with metals. HA-metal binding is of great importance at Cu post-flotation tailings due to extremely high As and Cu concentrations [3] and this problem should be emphasized in future investigations.

CONCLUSION

Investigated TC HAs humic belong to the type B pointing out to its lower humification degree. Bacis units at pH10 are in the 11.7-26.8 nm range. Pronounced reaggregation (1462-5218 nm) at pH3 points out to less expressed humic acid sol stability, as well as to increase in aromatic condensation degree. ZPs are obviously negative for all HAs at both pHs (-22.7 to -31.9 mV at pH10 and -16.3 to -19.4 mV at pH3). Correlation between particle size and E_4/E_6 index at pH10 indicates clear difference between Technosol humic acids and all control samples due to significantly lower degree of aromatic condensation. Under acidic conditions pronounced aggregation and increase in aromatic condensation of Technosol humic acids are obvious. Results obtained in this study unambiguously have shown changes in Technosol humic acid structure and properties with pH, which likely affect their interaction with metals. The present study precedes future investigations of humic acid binding to metals present at high concentrations in these Technosols.

ACKNOWLEDGEMENT

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CHLORINATION AS AN ALTERNATIVE FOR THE TREATMENT OF METALLIC SULFIDES AT LOW TEMPERATURE

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Abstract

The reaction tests of copper concentrates and several metallic sulfides with chlorine are carried out using thermogravimetric analysis (TGA) and isothermal conditioning in a horizontal reactor. The effects of the gas flow rate, temperature and chlorine content of the gaseous mixture (Cl_2+N_2) on the reaction rate are investigated. Starting materials and the solid reaction products are studied by scanning electron microscopy (SEM), X-ray diffraction (XRD) and chemical analyses. The selected sulfides started to react with chlorine from room temperature, producing respective chlorides. Complete reaction is achieved around 300 °C and the iron and sulfur chlorides are fully volatilized. The chlorination residues of the copper concentrates are composed of valuable metals chlorides ($CuCl_2$, $PbCl_2$, $ZnCl_2$) and unreacted gangue minerals. The treatment at higher temperatures allowed partial volatilization of $CuCl_2$ as well as its decomposition into CuCl. The suggested approach could be considered as an attractive route for the treatment of low-grade sulfide ores and concentrates and for the extraction of metals from slags and solid residues containing the targeted metals.

Keywords: Metallic sulfides, Chlorination, Temperature, Metal extraction

INTRODUCTION

The primary production of copper, zinc and lead is mainly provided through processing of sulfides ores and concentrates, where the main minerals are $CuFeS_2$, ZnS and PbS, respectively. Extractive metallurgy of these metals includes at least one pyro-metallurgical step releasing sulfur oxides (SO_x). Despite the technological improvement and strict control focused on SO_x emissions, the metallurgical processing of metallic sulfides is still a serious environmental drawback. This item is more pronounced for copper industry since 80 % of Cu are extracted from copper-iron-sulfur minerals by pyro-metallurgical processes. The progress on the end-of-pipe treatment for the conversion of sulfur oxides into sulfuric acid is the most preferred solution for the metallic sulfides sector. However, several plants, all over the world, still for economic or technical reasons, unload part of generated sulfur oxides to the atmosphere. In addition, the fugitive gas leaks, the acid transportation cost and the state of the sulfuric acid market push the metallurgists and researchers to design new flow - sheets for the metallic sulfide treatment. Growing demand for the metals, while the high-grade deposits are depleted or being exhausted also supports this trend.

Hydrometallurgical route is suggested by Habashi [1] offering the possibility of obtaining sulfur at moderate temperature and pressure thus solving the sulfur problem of sulfides treatment. Chlorination is also tried as an efficient alternative to recover the copper from its sulfides at relatively low temperatures. Donaldson and Kershner [2] studied the chlorination of $CuFeS_2$ by Cl_2 between 25 °C and 300 °C in a horizontal experimental set. They indicated that chlorination of $CuFeS_2$ started at 150 °C and was almost complete at about 250 °C generating copper and iron chlorides. Landsberg *et al.* [3] used the thermogravimetric analysis to study the chlorination of $CuFeS_2$ by Cl_2+Ar between 25 °C and 300 °C. They suggested that the formation of a product layer, at about 200 °C, slows down the reaction rate that is controlled by diffusion. Kumar *et al.* [4] performed the chlorination of a $CuFeS_2$ concentrate in powder and pellet form by Cl_2 between 400 °C et 550 °C using TGA. They suggested a flow - sheet for the extraction of copper, iron and other by-products from chalcopyrite. The proposed process is estimated to have an energy requirement of approximately 1780 kWh/ton of cathode copper, about one-half of the energy needed by the conventional hydrometallurgical processes. Other potential findings related to the use of chlorine for the treatment of various metallic materials and for the chemical synthesis are already reported in our previous research works [5-12].

This paper summarizes laboratory experimentations of chlorination process developed for two copper concentrates with a significant difference in valuable metal (Cu, Pb, Zn) content. The effects of several experimental parameters are studied in order to achieve a selective separation of the concentrate constituents.

MATERIALS AND METHODS

Two copper concentrates originating from European flotation plants were used here. The first concentrate contained (in wt):10.8% Cu, 29.7% Fe, 24.0% S, 0.8% Zn, 1.3% Ca, 6.7% Si, 2.1% Al and 1.2% Mg, and due to its low copper content is called "low grade copper concentrate - LGCC". While the main elemental content of the second sample is: 28.3% Cu, 26.3% Fe, 32.1% S, 4.3% Zn and 3.9% Pb, and it is designated as "high grade copper concentrate - HGCC" because of the total valuable metal (Cu, Zn, Pb) content is around 36.5%. The results of X-ray diffraction (XRD) showed that the LGCC contains $CuFeS_2$, FeS_2, SiO_2 and $(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$ (clinochlore) as the main crystallized phases. The principal identified phase in the HGCC is $CuFeS_2$. However, other mineral phases such as: PbS, $PbSO_4$, $Pb(Cu,...)_3(SO_4)_2(OH)_6$ and ZnS are also revealed by XRD in this concentrate.

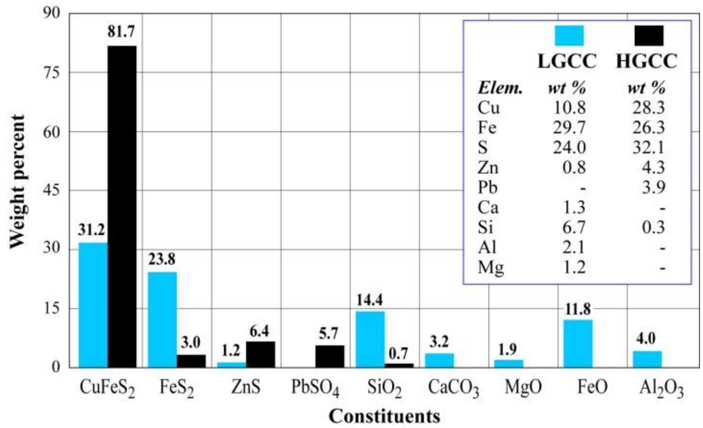

Figure 1 *Elemental and phase composition of the copper concentrates*

Based on the results of scanning electron microscopy (SEM), XRD and chemical analysis, a calculation of the phase contents of both the concentrates is given in Figure 1. Clearly, the major sulfides of the LGCC were $CuFeS_2$ and FeS_2. The high pyrite content in this concentrate is probably due to the ineffectiveness of the physical separation processing. The LGCC gangue is essentially composed of quartz and clinochlore. The HGCC was rich in chalcopyrite (81.7%). Moreover, it contained some amounts of lead and zinc compounds, while its gangue content was low. The particles size measurements indicated that d_{50} is 85 and 35 µm for the LGCC and HGCC, respectively and they have a mean specific surface close to 0.63 m^2/g. Besides industrial concentrates, the selected minerals ($CuFeS_2$, ZnS, PbS, FeS_2) as well as S° used for this study were of natural origin. The SEM and XRD analyses are used to check their compositions.

The Thermogravimetric analysis (TGA), described early [5], is used for the first experimental tests of non-isothermal sulfides chlorination, while the horizontal experimental set-up [5] is used to carry out isothermal tests to chlorinate the targeted sulfide materials under different conditions. This apparatus assembly is composed of a gas-metering unit followed by a gas purification item and an electric furnace. Passing the gaseous mixture (Cl_2+N_2) through a carbon furnace eliminates any trace of oxygen. The gaseous reaction products are recovered through condensers and the outlet gases are purified before their release to the atmosphere. The solid reaction products are examined by SEM, XRD and chemical analyses to evaluate the kinetics and the efficiency of the chlorination process.

RESULTS AND DISCUSSION

Non-isothermal chlorination of metallic sulfides

TGA of both the concentrates under Cl_2+N_2 (Cl_2/N_2 = 1) are carried out up to 1000 °C. The major constituents of these concentrates ($CuFeS_2$, ZnS, PbS, FeS_2) as well as S° are also treated in the same conditions. Results are depicted in Figure 2 as percent mass loss (% ML) of the samples as a function of temperature. A rough examination of the obtained data suggests that the chlorination of the chalcopyrite started from room temperature. The mass gain observed up to 300 °C is due to the intensive chlorination of the $CuFeS_2$ sample generating $CuCl_2$, $FeCl_3$ and sulfur compounds (S°, S_2Cl_2 and SCl_2).

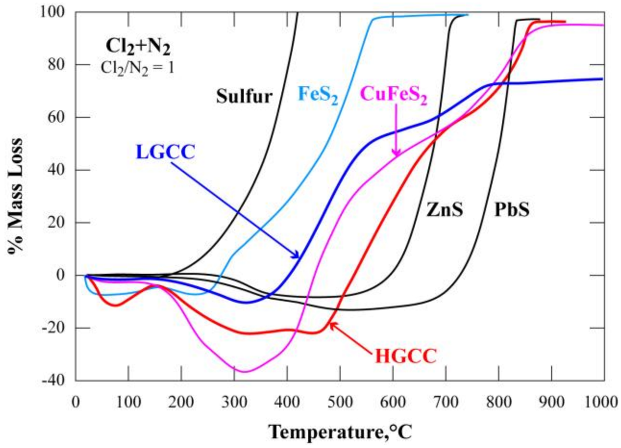

Figure 2 *TGA of selected metallic sulfides and two concentrates in* Cl_2+N_2

Then, the volatilization of ferric chloride ($FeCl_3$) could be the responsible of the % ML observed up to about 475 °C. The slow-down of the mass loss between 550 °C and 700 °C may be explained by the partial volatilization of $CuCl_2$ and its decomposition into cuprous chloride (CuCl), followed by the volatilization of CuCl (Cu_3Cl_3) at higher temperatures. The main %ML of the FeS_2 sample at temperatures higher than 250 °C are attributed to the volatilization of the gaseous ferric chloride. The behavior of $CuFeS_2$, FeS_2 (producing $FeCl_3$ and S_xCl_y) and S° (generating S_xCl_y) and the shape of their respective % ML curves seem to be in good agreement with the vapor pressure of the selected chloride, as shown in Figure 3. The shift of the temperature towards high value in the TGA curves is attributed to the fact that the tests are performed in continuous temperature rise with relatively high heating rate (25 °C/min). Lead and zinc sulfides started to react with Cl_2 at temperature higher than 200 °C and the mass gains recorded at low temperatures are due to the formation of lead and zinc chlorides. Since then, the % ML at high temperatures (600 °C for the ZnS and 700 °C for PbS) can be explained by the volatilization of $ZnCl_2$ and $PbCl_2$ (Figure 3).

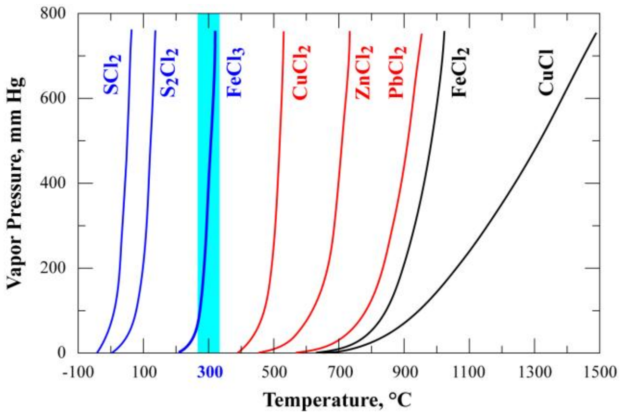

Figure 3 *Evolution of the vapor pressure as a function of temperature for several chlorides*

As shown on Figure 2, the curve of the LGCC chlorination gathered the characteristics of the $CuFeS_2$ and FeS_2 chlorination curves, what is in good agreement with the composition of this concentrate containing 31.2% $CuFeS_2$ and 23.8% FeS_2 (Figure 1). About 75% of the sample are chlorinated and volatilized at 1000 °C. The final residue was essentially composed of Si, Al and Mg oxides. The chlorination behavior of the HGCC was close to that of the chalcopyrite. The high content of $CuFeS_2$ (81.7%) in this concentrate explains this similarity. More than 95% of this concentrate are chlorinated and volatilized around 850 °C.

Isothermal chlorination of copper concentrates

After an investigation of the effects of the gas flow rate and chlorine content on the reaction kinetics of the metallic sulfides, attempts were made to know the effect of temperature on the chlorination of LGCC, HGCC, $CuFeS_2$, FeS_2, ZnS and PbS. Only results related to the LGCC and HGCC chlorination from 20 °C to 700 °C in Cl_2+N_2 (Cl_2/N_2 = 1) for a reaction time of 2 hours are given here.

Table 1 summarizes the phases identified, by XRD, in the chlorination residues of LGCC at different chlorination temperatures. The chlorination residue of LGCC at 300 °C is composed of $CuCl_2$, clinochlore and quartz. Higher temperatures of the chlorination allow the transformation of clinochlore, volatilization and/or decomposition of $CuCl_2$. Although the decomposition of $CuCl_2$ into CuCl must occur at about 540 °C, its partial decomposition is due to the high partial pressure of chlorine in the chlorination process. In addition to copper chlorides, the chlorination residues obtained at 700 °C contain quartz and silico-aluminates that can be environmentally friendly. The XRD results for the HGCC chlorination residues suggested nearly similar phenomena to those observed for LGCC. At 300 °C, the chlorination residue is mainly composed of the Cu, Zn and Pb chlorides and they remain partially in the residue resulting from the treatment at 700 °C.

Table 1 *Phases identified by XRD in the LGCC chlorination residues up to 700 °C*

Phases	Raw	20 °C	50	100	150	200	250	**300**	400	500	600	700
$CuFeS_2$	■	■	■	■	■	■	▨					
$CuCl_2$		■	■	■	■	■	■	■	■	■	■	▨
CuCl											▨	■
FeS_2	■	■	■	■	■	■	▨					
$FeCl_3$		▨	▨	▨	▨	▨	▨					
Clinochlore	■	■	■	■	■	■	■	■	■			
SiO_2	■	■	■	■	■	■	■	■	■	■	■	■

■ Identified phase ▨ Probable phase

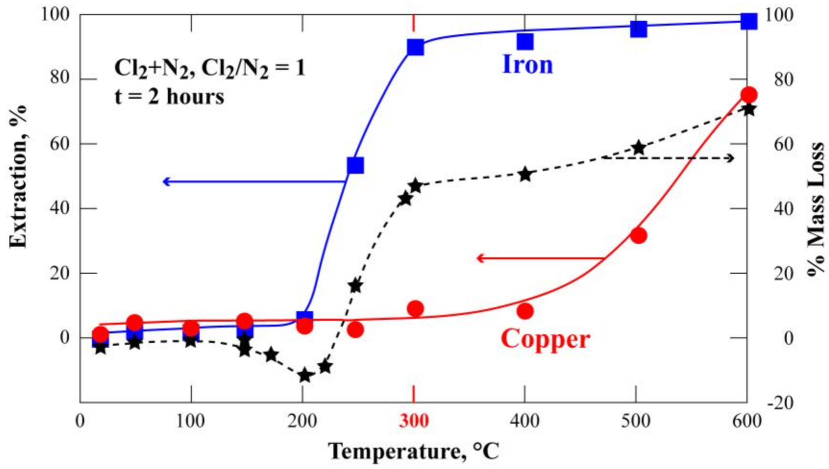

Figure 4 *Results of the chlorination of the LGCC*

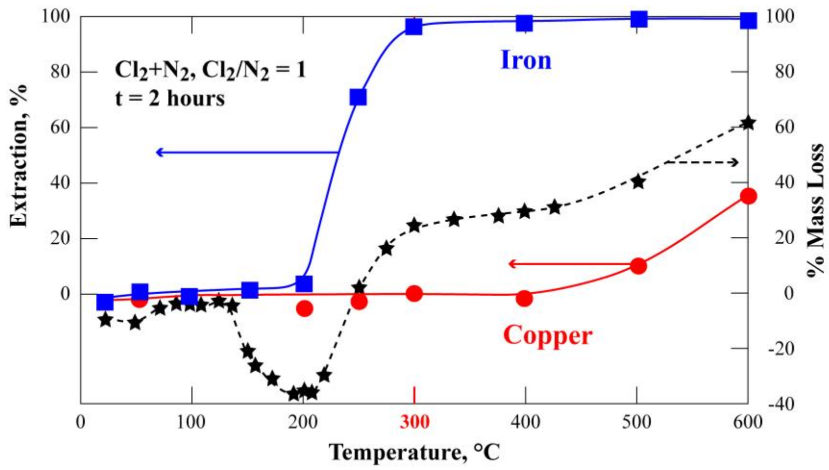

Figure 5 *Results of the chlorination of the HGCC*

Comprehensive results for the chlorination of LGCC and HGCC are summarized respectively in Figures 4 and 5. These figures gather the extraction extent of copper and iron with the %ML of the samples. As shown on Figure 4, iron extraction of LGCC is significant from 200 °C but it is not complete at 300 °C because of the inert nature of the iron present in clinochlore; full extraction of iron could be achieved at T > 500 °C where the clinochlore is decomposed. Copper extraction became significant at temperature higher than 400 °C and about 75% of copper were extracted at 600 °C. The %ML curve traced in Figure 4 for the LGCC chlorination are in good agreement with the extraction extents of iron from 200 °C and of copper from about 350 °C.

Almost full iron extraction is achieved at 300 °C during HGCC chlorination (Figure 5) what agrees with the presence of all iron as sulfides. The copper extraction started at higher temperatures than in the case of LGCC and only about 40% of Cu are extracted at 600 °C. This is probably due to the fact that the HGCC residues are systematically agglomerated whilst those of LGCC did not undergo such a behavior. The presence of inert compounds in LGCC, such as SiO_2, prevented the agglomeration of the chlorination residues. This is one more raison to use chlorination for the treatment of low-grade ores and/or concentrates.

CONCLUSION

The reaction of the selected metallic sulfides with chlorine started from room temperature and the process was intensified at temperatures of the significant volatilization of the generated chlorides. Under non-isothermal conditions, the complete chlorination of the targeted sulfides and volatilization of the reaction products can be classified in decreasing order: $S > FeS_2 > CuFeS_2 > ZnS > PbS$.

The selective separation of iron and sulfur chlorides from those of valuable metals was possible during the chlorination of the chalcopyrite concentrates at 300 °C for a reaction time shorter than two hours. More than 95 % of copper were concentrated in a treatment residue free from iron and sulfur. The selectivity of the chlorination process was assured by the large differences of the vapor pressure between the chlorides of valuable metals and those of sulfur and iron.

This research work is developed as an alternative to the pyro-metallurgical technology for the treatment of the low-grade sulfides at low temperature without sulfur oxide emissions. It can also be used for the extraction of metals from slags and solid residues containing the targeted metals.

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THE COMMON POPULATION SIGNAL IN THE EUROPEAN ASH (*Fraxinus excelsior* L.) TREE-RING CHRONOLOGIES IN NP \`DJERDAP\` SERBIA

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Abstract

The aim of this study was to establish tree-ring chronologies of European ash in the area of National park \`Djerdap\` and to evaluate the strength of the common population signal imprinted in the radial growth of the trees of this species. For this purpose almost a hundred cores were taken from the dominant trees at three distant locations where the tree growth was driven by different ecological conditions. The characteristics of the studied tree-ring series and the strength of the common growth response of trees within the sites were determined by using several dendrochronological and statistical parameters. Subsequently, the temporal stability of the Expressed-Population-Signal (EPS) was examined by applying moving windows. Furthermore, the presence of the common variability between the site chronologies was studied by means of t-test and Principal component analysis. It was concluded that the obtained site chronologies have sufficient population signal that can be processed in future as a proxy for dendroclimatological surveys. However, considering the length of the obtained chronologies and the level of their mutual agreement, an additional sampling should be performed in order to extend the chronologies back in time as well as to enlarge the network of investigated sites.

Keywords: Dendrochronology, European ash, NP \`Djerdap\`, Common population signal

INTRODUCTION

Valuable broadleaved tree species of Serbian forests are mostly found in beech forest communities, in small groups or as mingled trees [1]. The fact that this group of deciduous trees are still referred to as \`other hard broadleaved trees\`, in the management plans shows that they haven\`t been given enough attention, even though their economic, ecological and esthetical importance has been indicated for a long time now [2-7]. According to Drachenfels *et al*. [8], mixed forests of beech and valuable broadleaves are classified as European forest communities richest in woody species.

One of the most significant species of valuable broadleaved trees is European ash (*Fraxinus excelsior* L.). Its potentially high economic and ecological value, as well as its rapid growth increase in youth and attainment of significant dimensions in a relatively short time period have caused an increased interest in this tree species in the last decades [9,10]. However, the recent severe crown dieback has caused great concern for the future of ash in many parts of Europe [11]. The dieback of ash has been recorded in many countries in Europe [12-14], seriously endangering the existence of this tree species. Unambiguous symptoms of ash dieback disease have also been observed in Serbia [15].

Apart from pathogens, the spreading dieback of European ash has also been related to climatic changes [16]. Generally, the research of radial growth (increment) of trees and stands, as unique bio-indicators of their vitality and health, are of particular importance in the study of the effects of climate and other biotic and abiotic factors on forests and forest ecosystems [17]. For this purpose, dendroclimatological studies, which are largely based on quantitative analysis of radial increment and its dependence on various climatic elements, are particularly suitable and very useful. In order to obtain valuable information from such studies, the procedure of radial increment chronology production represents the first step and `the backbone` of every tree-ring research. Due to the previously mentioned facts, the main objectives of the study were (1) to define the master chronologies of European ash for investigated sites in the area of `Djerdap` National Park, (2) to determine the strength of the common population signal within the investigated sites and (3) to analyse teleconnection between the established chronologies.

MATERIAL AND METHODS

For the purposes of dendrochronological analysis, 43 European ash trees with largest diameters were sampled from three mixed beech-valuable broadleaved stands grown on acid or luvic acid brown soils. Climate conditions of investigated sites are characterized by the average annual precipitation of 784 $mm \cdot m^{-2}$, which is above the average annual precipitation in Serbia (734 $mm \cdot m^{-2}$) for the period 1961–1990 [18] and the average annual air temperature of 11.2 ^{o}C (1955-1991). Further information on ecological and geographical characteristics of the investigated stands is given in Table 1.

Table 1 *The main geographical and ecological information about the studied stands*

Site	Latitude	Longitude	Elevation (m)	Aspect	Soil type
LR32	E44° 34'	N21° 56'	707-729	SE	Acid Brown
KO30	E44° 35'	N21° 59'	534-555	W	Luvic Acid Brown
SK57	E44° 37'	N22° 17'	440-463	EW	Acid Brown

The values of raw radial increment were determined using an LINTAB device to the nearest 0.01 mm. The ring widths were cross-dated visually by using strikingly narrow and wide tree rings and curve sliding and overlapping of in TSAP software. Further data processing was performed using dendrochronological library dplR in R environment [19,20]**Error! Reference source not found.**. During the additional synchronization, guidelines given by Bunn [21] were used, according to which the series were compared with the master chronology in 40-year segments, half of which overlap. To avoid fixation, the segments were postponed over the chronologies, so that the synchronization covered all edge portions. Finally, the similarity between the tree-ring curves was evaluated by calculating the *Gleichläufigkeit* coefficient (Glk) and t-test (t_{bp}) value after Baillie and Pilcher [22].

The mean sensitivity (MS), autocorrelation (AC1) and some other dendrochronological parameters were calculated from the year when the sample replication was at least a 4 tree-ring series. Each particular chronology of radial increments was fitted with a cubic smoothing spline with a 50% frequency response at 67% of the series length. Ring-width (radial increment) indices were computed by dividing each empirical radial increment value of a year by the fitted value of that year. Furthermore, the standardized series were averaged within sites to obtain standard (STD) master chronology by applying a bi-weight robust estimation of the mean value function [23]. In order to remove autocorrelation, chronology was prewhitened by autoregressive modelling and the residual (RES) master chronology was constructed. The strength of the common signals in the developed master chronologies are expressed using the common indicators: Expressed population signal – EPS [24,25], Signal-to-noise ratio – SNR [25] and percentage of variance explained by the first principal component (PC1). Temporal stability of EPS (Subsample-signal-strength-SSS) was inspected by 40-year running window moved across the chronologies in one-year steps. In addition, the teleconnection between the obtained residual site chronologies were assessed with both Glk and t_{bp}, while more detailed analyses of shared variance were performed with PCA.

RESULTS AND DISCUSSION

The results of the measurement and data analysis of the European ash radial increment series are given in Table 2. The appropriate selection of the final sample which should contain a sufficient value of the common signal in growth represents the first and basic step in the dendrochronological research [26]. Therefore, the applied multiple synchronization procedures reduce the sample to 68 series of radial increment, with an average length ranging from 54 to 88 tree rings. The mean ring width values (i_r) in definite sample range from 2.38 to 3.56 mm, with the standard deviations (SD) up to 1.59. The average values of Glk (65-71) and t_{bp} (4.52-5.55) coefficients are above the generally accepted thresholds indicating a satisfactory degree of similarity between the obtained curves. It is also worth noticing that both average values of the mentioned parameters are quite higher for the series from SK57 probably because it is comprised of only 7 trees. As an additional measure of interdependence, we determined the series intercorrelation (r_{xy}) representing the average correlations of individual series with master chronologies. The resulting mean values are between 0.71 and 0.74 and according to Grissino-Mayer [27] belong to the group of common values of these indicators for most chronologies. Therefore, the analyzed parameters confirm that definite samples per sites are well-selected and composed of a series of similar radial increment patterns.

Table 2 *The main dendrochronological features of tree ring series from investigated sites*

	Number of		First	Last	Average series							
	trees	cores	year		length	r_{xy}	Glk	t_{bp}	i_r [mm]	SD	MS	AC1
LR32	19	32	1928	2014	77	0.71	65	4.52	2.57	0.95	0.22	0.66
KO30	13	22	1920	2015	88	0.74	65	4.59	2.38	1.24	0.25	0.70
SK57	7	14	1952	2015	54	0.72	71	5.55	3.56	1.59	0.31	0.56

The determined amounts of AC1 range from 0.56 to 0.70, indicating that the interdependence between consecutive years is very strong. Although some publications negatively discuss the possibility of using MS as a measure of series sensitivity [28], we chose to analyse this parameter. The recorded values for empirical series range from 0.22 to 0.31 and as instructed by Grissino-Mayer's [27] belong to the group of middle sensitive (LR32 and KO30) and sensitive series (SK57).

The main statistical and dendrochronological properties of the developed site chronologies are given in Table 3a. In comparison to the raw series, the values of MS are noticeably reduced after averaging tree ring indices into STD site chronologie.

Table 3 *The basic statistics (a) and teleconnection analysis (b) of developed site chronologies*

a)	Site chronology	length	MS	AC1	EPS	SNR	PC1	b)	Δ dist. [km]	Δ alt. [m]	Glk	t_{bp}
1. LR32	STD	87	0.16	0.50	0.95	18.28	0.50	**1 vs 2**	3.8	173.5	60	4.76
	RES	86	0.18	0.07	0.94	16.54	0.47					
2. KO30	STD	96	0.17	0.38	0.90	9.04	0.42	**2 vs 3**	23.8	93.0	64	5.46
	RES	95	0.20	-0.06	0.90	8.82	0.40					
3. SK57	STD	64	0.27	0.14	0.88	7.57	0.56	**3 vs 1**	27.7	266.5	76	5.46
	RES	63	0.32	-0.13	0.90	8.86	0.56					

However, the additional removing of low-frequency through prewhitening leads to the increased mean sensitivity of RES chronologies. Generally, the most sensitive but the shortest chronologies are developed for site SK57. We also found that population signals are considerably expressed (0.88-0.95) across the studied locations and the signal-to-noise ratio is double higher for LR32 chronologies than for the chronologies from the other two sites. The variance explained by PC1 ranges between 40% and 56%. Altogether, the obtained results indicate that the largest part of variations in the analyzed series of radial increment was caused by the common response of trees to the prevailing growth conditions.

An insight into the teleconnection revealed that the data from the remotest sites SK57 and LR32, with the biggest altitudinal difference (Table 3b), have the best mutual matching according to both calculated indicators (Glk=76; t_{bp}= 5.46). The same values of t_{bp}, but a slightly lower Glk was determined for SK57 and KO30, while the lowest level of similarity was ascertained for just 3.8 kilometres distant KO30 and LR32 chronologies. All in all, the established site chronologies show a substantial degree of agreement.

The curves of site chronologies and temporal stability of EPS are presented in Figure 1a. Since the signal strength can vary through time and it is also strongly dependent on the sample depth, the computation of EPS in moving sequences could be a very useful procedure to determine a well-replicated part of the chronologies with sufficiently expressed common signals. As is shown, the population signal within sites is quite stable and constantly above the conventionally adopted threshold (0.85) in the whole study period. The chronologies established in such a way are particularly suitable for the further investigation of the environmental impact on radial growth. An additional analysis of common variation structure for the site chronologies showed that three principal components account for 66%, 18.4% and 15.6% of the common variance, respectively (Figure 1b).

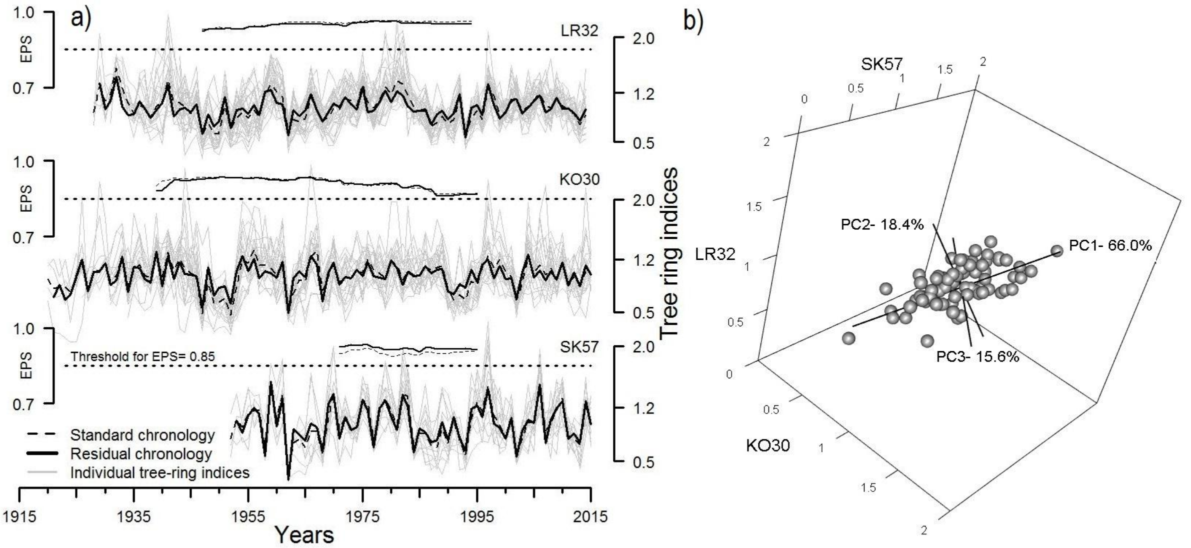

Figure 1 *a) Individual tree-ring indices, standard and residual site chronologies and values of running EPS; b) The structure of common variation between site chronologies explained by principal components*

CONCLUSION

The European ash of the studied sites showed good crossdating possibilities. The obtained results indicated that the analyzed samples displayed a required level of synchronization at the site scale. The most pronounced agreement and the highest mean sensitivity recorded for the samples were included in the SK57 data-set. Following the principle of a collective population response, the quality and reliability of the common growth signal was enhanced by the averaging series of the tree-ring width into the site chronologies. The most expressed population signal and the highest signal-to-noise ratio were determined for LR32. The common signal was quite strong in all three studied chronologies and quite stable over the study period. Furthermore, the presence and the structure of the common growth response among developed site chronologies were also investigated. On the whole, the mutual teleconnection is very pronounced, especially between the sites with the same soil type, even though SK57 and LR32 are geographically most distant. Having that in mind, it can be concluded that the radial growth on the studied sites is predominantly controlled by the governing climate conditions, which represent the only environmental component that could have a more or less uniform influence on such big area. In addition, it was determined that the largest portion of the common variability between site chronologies lies along the first principal component.

The obtained site chronologies of European ash have sufficiently expressed population signals in tree-rings series that could be processed for further dendroclimatological surveys. In the light of the general concern for the future of this species, it is of particular importance to understand the past and to consider the future climate impact on the growth of this species, especially in relation to the dieback disease. Furthermore, the herein reported interdependence between the studied site chronologies suggests the possibility of forming the European ash chronology at a wider scale, thus enabling us to expand the frameworks in which the conclusions are valid. Nevertheless, to provide more reliable results, it is necessary to conduct additional sampling of additional European ash stands and to form a network of investigated sites on the whole area of NP `Djerdap` as well as to extend the length of the established chronologies.

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ENVIRONMENT PROTECTION AT DRENOVACA LIMESTONE MINE NEAR PRIJEDOR

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Abstract

The focus of this paper is on significance of exploitation, preparation and processing of non-metallic mineral raw materials as a recourse that could significantly contribute to economic development of developing countries. In order to achieve this goal the application of new technologies in mineral processing should be considered as an indicator of sustainable development with special consideration given to protection of environment. The fundamental technological solutions are focused on air protection (system of dust removal in limestone preparation plant), but in some project solutions and in the stage of manufacturing the imperative is on ground water protection as well as degraded soil re-cultivation. These tendencies also give a chance for development of authentic and efficient technological solutions.

Keywords: Non-metallic raw materials, Limestone fillers, New technologies, Indicators of sustainable development, Environment protection

INTRODUCTION

Prijedor region needs for technical building stone by the end of 1970ies have initiated reviewing of possibilities of opening of more solid raw materials base with adequate quality characteristics. Until then the concrete manufacture for construction sector was based on the exploitation of gravel and sand from the riverbed of Sana river, and from alluvial deposits in Prijedor alluvial plain, with all the negative consequences to the environment. The deposits of technical building stone in the Drenovaca mine are located on southern slopes of Kozara mountain.

Department of geology of Iron Ore Mine Company ‘Ljubija’ has done complete geological surveys of this locality. The survey, research, and reserves estimate has been done in 1982. The limestone of ‘Drenovaca’ deposit has been verified as a raw material to be used in manufacture of aggregate for concrete, lower load-bearing layers on roads of all categories, concrete load-bearing layers on roads of all categories, and as a possible raw material to be used as breakstone for the railway. The possibility of application in sugar manufacture and metallurgy has been found. Based on these findings the mine (quarry) has been designed and built as well as the crushing, grinding, classification, and manufacture plant, according to market requirements. After analysis of the possibilities of application of this limestone as filler, the system for air dust removal has been built. During the limestone manufacture in ‘Drenovaca’ mine the special attention has been given to the problem of ground water protection, because there is a source of drinking water in the vicinity that is being used for the water supply of nearby villages.

PROJECT BASED SOLUTION

Based on the quality of limestone in this deposit, and market needs, the preparation plant project has been done. The initial project has predicted only primary crushing and grinding along with separation of tailings and classification of pure limestone according to size class for building industry use (-60+32 mm, -32+16 mm, -16+8 mm, -8+4 mm, -4+0 mm).The removal of dust from primarily crushed limestone has been introduced. This solution and installed equipment did not provide expected quantities and the quality of product for the market. Thus the decision has been made to introduce secondary crushing and grinding of the class size -60 + 32mm, and classification in the closed cycle with the goal to get larger quantities of smaller product classes which were needed in the market. Later on during the operation of the plant has been proven that there is also a need to introduce the tertiary crushing, grinding, and classification in order to produce larger quantities of class size -4 +0mm.

AIR DUST REMOVAL SYSTEM

Air dust removal system integrated into ‘Drenovaca’ limestone preparation mine had a sieve that was used after primary crushing and grinding, and also had dust removal facility for secondary grinding, crushing and classification. The air dust removal system contains dust removal equipment, transportation of limestone dust to the silo, and the system of emptying the silo. The air removal system schematic is shown on Figure 1.

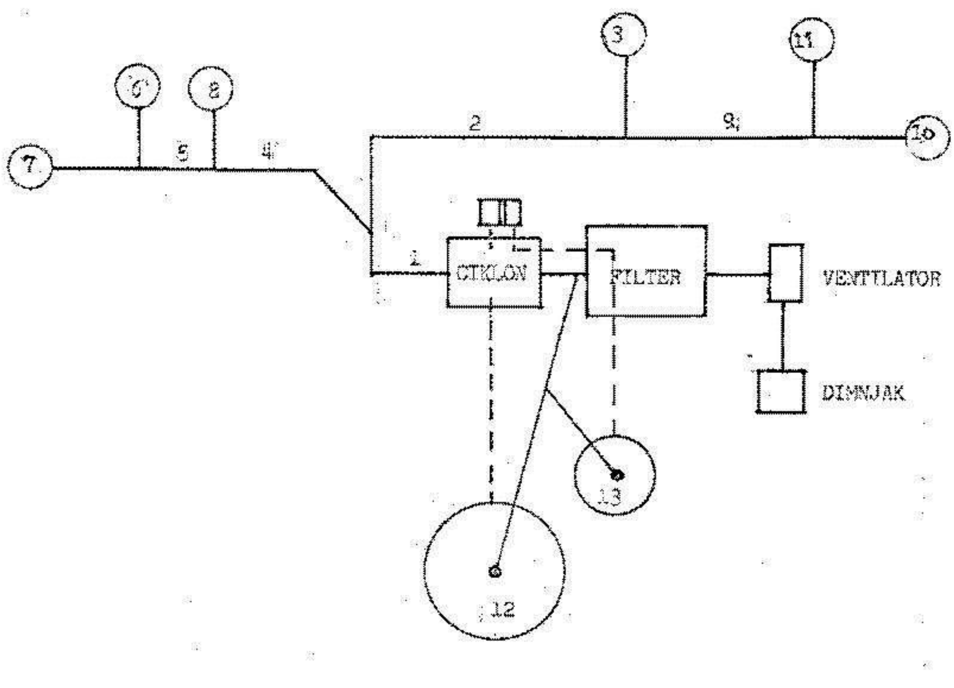

Figure 1 *Air dust removal system*

Figure description:

"DIMNJAK"- chimney, "VENTILATOR"- fan, "FILTER"-filter, "CIKLON"- cyclone

The following equipment has been installed in the air dust removal plant:

1. Multi-cyclone battery Ø 250 / 34
2. Bag shaped dry filter SVF-420
3. Centrifugal fan CV9
4. Two silos, pipelines, elbows, reduction valves, regulatory butterflyvalves, chimney, etc.

Air dust removal process

The dust that is made in the technological process of limestone preparation is vacuumed away from the machines through the pipes. The amount of air that is being used in this process is determined on the basis on equipment manufacturers recommendations. The amount of vacuumed air is regulated with regulatory valves which have been installed at each place were the dust is removed. The pipes have been designed in a way that the air speed inside them is sufficient to prevent the settling of dust. The vacuum pipes are connected to the central collector pipe, which is connected to the cyclone battery. There are rubber sealants at the pipes joints, which are used for sealing and soundproofing.

The cyclone battery Ø 250 / 34 is made out of 34 cyclones with 250mm diameter each, in which 90-95% of dust is separated. The air with the remaining dust goes into the bag shaped dry filter in which almost all the remaining dust is separated. This system has more than 99% efficiency, so that the dust concentration at the filter exit is below 50 mg / Nm^3, the maximum allowed concentration being 150 mg / Nm^3. The bag shaped filter is equipped with the programmed device for bag cleaning. The time for the device activation is set by the timer. The purified air from the cyclone battery and the bag shaped filter is released to the atmosphere via fan.

Dust transportation

Dust transportation is conducted in two separated silos. Dust from the multi-cyclone is injected into the pneumatic transport dosator through dispenser and is transported into a silo of 200t capacity. Dust from the filter is transported into a silo of 50t capacity. On this line of pneumatic transport, there is imbedded pipe crossover with which is possible to transport the dust into a bigger silo, if needed. The air removal from the silo is done by connecting the upper roof chambers of the silo with the vacuum side of the filter via vacuum pipe, which solves the problem of dust removal in the silo. The maximum height of filter filling is controlled automatically. Emptying of the 200t silo into the systems is done with a manual device, and emptying of 50t silo is done with worm conveyor, which packs the dust into the bags.

Movement of materials schematics

Movement of material schematics is done according to technological schematics of the project where the input capacity is set to be 150 m^3/ h. During the many years of operation of this facility the achieved capacity was 80 m^3/ h, so the corrected schematics of movement of materials was used when the dust removal equipment needed to be chosen. The data for the making of schematics has been acquired by taking the samples from the facility and the technological processing. The recordings were made during the operation of the facility in the year of 2004 and 2005. According to the schematics the amount of limestone dust (-250+0 micrometers) which can be acquired through the dust removal process is 11 m^3/ h based on the achieved capacity of 5-6 m^3/ h.

The apparatus schematics

We did not deem necessary to show both material movement schematics and technological schematics of the whole facility because our experts are well acquainted with it. In this paper we have shown the schematics of dust removal and apparatus schematics, being convinced that this is quite sufficient for understanding of the concept of 'Drenovaca' mine dust removal system construction.

Figure 2 apparatus schematics:

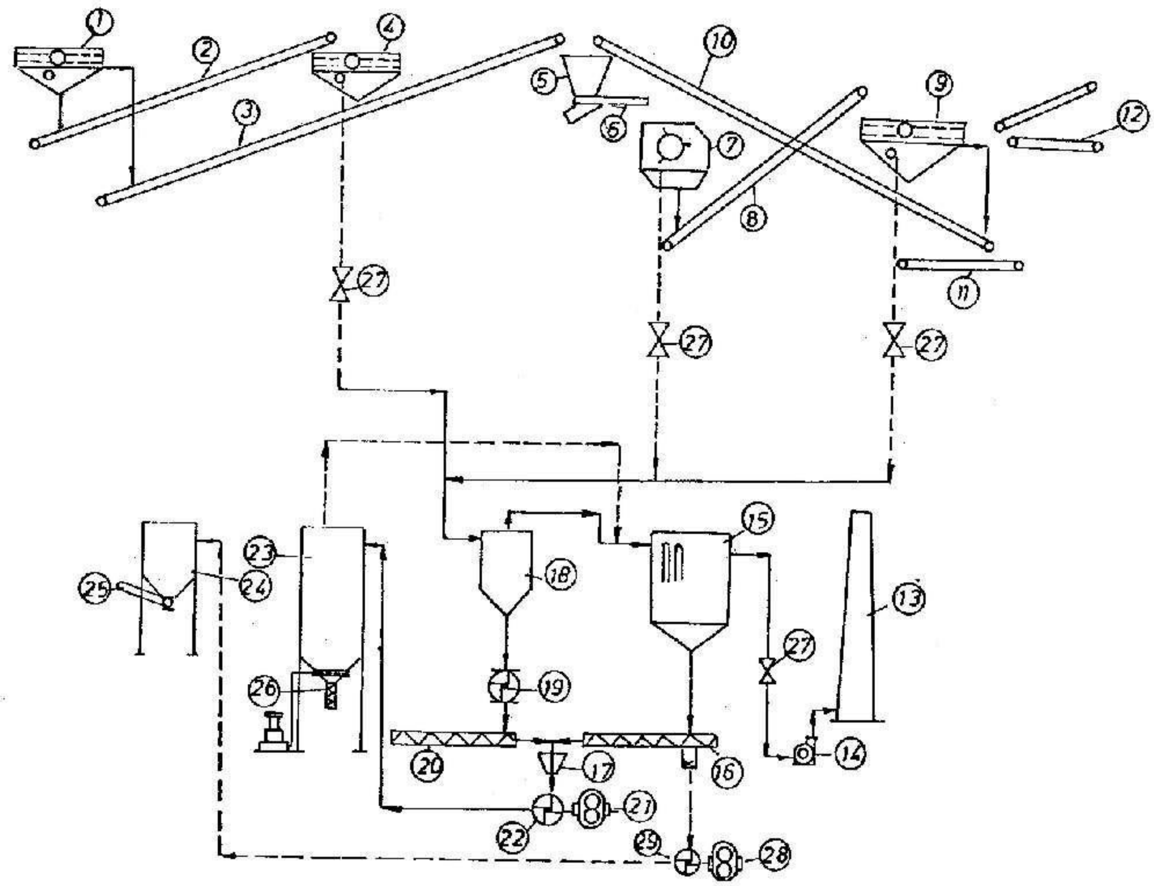

Figure 2 *The apparatus schematics*

Description:

◆ Installed basic equipment:

1. Vibrational sieve Rvg 7x2
2. Rubber conveyer belt B=500mm
3. Rubber conveyer belt B=600mm
4. Vibrational sieve Rvg 7x2
5. Bunker V=10m^3

6. Vibrational dispenser Q= 10-50 m^3/h
7. Impact grinder (secondary) MG-100; Q= 25 m^3/h
8. Rubber conveyer belt B=600mm
9. Vibrational sieve LOK-4
10. Rubber conveyer belt B= 400mm
11. Rubber conveyer belt B= 400mm
12. Rubber conveyer belt B= 400mm

◆ The existing equipment in the dust removing system:

13. Chimney
14. Centrifugal fan Q=36000 m^3/h
15. Bag shaped filter F=422 m^2
16. Worm conveyer
17. Compensating dish
18. Cyclone battery Ø 250

◆ New dust removal system:

19. Rotational butterfly dosator
20. Worm conveyer
21. Rotating compressor
22. Rotational butterfly dosator
23. Storage silo V = 200 m^3
24. Storage silo V = 50 m^3
25. Worm conveyer
26. Emptying system
27. Regulatory valve
28. Rotational butterfly dosator
29. Packaging machine

Capacity and assortment

Assortment of limestone filler in this process is composed of:

-asphalt filler according to JUS B.B3.045 standard

-filler for chemical and other branches of industry (99% of the particles – 32 micrometers)

According to the material movement schematics for the one year of operation with 1600 work hours in the ‘Drenovaca’ limestone mine dust removal system 3600t of asphalt filler are produced, as well as 400t of filler with 99% of 32 micrometer particles.

Market analysis has shown that complete production output of dust removal system can be distributed in the local market of asphalt production in the Prijedor region, as well as in agriculture for soil calcification and livestock food production.

Financial and economic analysis has shown that certain amount of profit can be gained on the limestone mine ‘Drenovaca’, near Prijedor, dust removal system, which means that construction of this system alongside with ecological has also economic justification.

CONCLUSION

1. Ever since the construction of ‘Drenovaca’ preparation facility there has been an environment protection problem, as well as the working environment protection problem because of the limestone dust emission into the environment.

2. In the first stage only the primary grinder dust removal system has been built, but the problem is more pronounced in the secondary crushing, grinding and classification section.

3. The technological analysis done at ‘ITNMS’ institute in Belgrade has shown that the limestone dust from the ‘Drenovaca’ mine with its chemical and physical-mechanical characteristics is fully compatible with the specifications of the branches of industry, which use carbonate fillers.

4. Technical and economic analysis has shown that is justified to install dust removal system at ‘Drenovaca’ mine.

5. The project based solutions and choice of equipment are based on contemporary scientific and professional achievements, and they are encompassing the effects which are in compliance of environment protection, and work environment protection standards.

6. Other than accentuated positive ecological effects, the dust removal system also brings positive economic effects to the company because the dust removal products have higher selling price than construction aggregates, and can easily be sold in the market.

7. Other than economic and ecological advantage the construction of dust removal system has contributed to the reputation of the company with business partners and local community, as well as the overall company status upgrade.

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ACCUMULATIVE RESPONSE OF SOAPWORT AND YARROW TO Cu AND As, ENHANCED BY Cu ORE MINING AND SMELTING COMPLEX: A MULTIVARIATE COMPARISON

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Abstract

In this paper, the results obtained during an examination of the copper (Cu) and arsenic (As) content in the root and shoot of soapwort (Saponaria officinalis L.) and yarrow (Achillea millefolium L.) from the Bor region are compared between each other with the aim of ascertaining if there is some difference in metal uptake by different plant species. In all the samples the content of Cu and As was determined using inductively coupled plasma optical emission spectrometer (ICP-OES Optima 8300; Perkin Elmer, USA). The results obtained by multivariate techniques such as the Principal Component Analysis and Pearson correlation analysis confirmed that very useful information was recorded in these plants. Precisely, both plant species may be recommended as suitable plants for phytostabilization purposes.

Keywords: Excluder, Soapwort, Yarrow, The Bor region

INTRODUCTION

Mining and pyrometallurgical production of copper is greatly affecting the nature and ecosystem and are often referred to as one of the biggest polluters [1,2]. The negative influence of Mining and smelting complex can be seen through degradation of the environment of Bor and the Bor region. Hence, the emission of fine particles and volatile oxides of heavy metals from the chimneys of the copper smelter represents a major pathway for heavy metals to reach the atmosphere, soil and biosphere, which is documented by numerous studies [3-6]. For this reason, long-term biomonitoring provides certain data for environmental risk assessment of the examined area by measuring the concentration of metals/metalloids in different parts of various plant species, thus representing a potential candidate for photoremediation [7]. Also, a large number of plant and soil samples was analyzed in order to obtain useful data on the distribution and source of pollutants in the examinened area [8]. In the investigated area, two types of herbaceous plant species (soapwort and yarrow) were sampled and analyzed together with the soil from seven studied sites (FJ, BN, SN, NS, O, S and M) in the autumn of 2015. In this paper, by interpreting the results of Pearson's correlation and PCA analysis, the answers about the origin of the examined elements and their uptake in the investigated plant species were obtained. The obtained results will give us important information on the potential of yarrow and soapwort as indicators, excluders or accumulators for the analyzed elements Cu and As.

MATERIALS AND METHODS

The samples (soil, root, shoot) were collected from the sampling sites which are closest to the main source of pollution, such as the copper smelter, and includes the urban-industrial zone: FJ (Flotation tailings pond), BN (Bolničko naselje), SN (Slatinsko naselje) and NS (Naselje Sunce); the rural zone: O (Oštrelj) and S (Slatina), with more details in Dimitrijevic et al. [4]; and the control zone M (Minićevo). Minićevo is an unpolluted area which is located 45 km from the town of Bor. At all the studied sites, the root and shoot of soapwort and yarrow were sampled, as well as the soil (0-30 cm) on which the mentioned plant species grow. The dried material was ground in a laboratory mill, homogenized and stored until further analysis of the samples. For the determination of heavy metal content, each sample was digested in a microwave digestion system ETHOS 1 according to the US Environmental Protection Agency [9]. The concentrations of Cu and As were determined using inductively coupled plasma optical emission spectrometer (ICP-OES Optima 8300; Perkin Elmer, USA). The pH meter (pH), electrical conductivity (EC), and organic matter (OM) of soils were determined using standard methods according to a previous paper by Nujkić *et al*. [5].

The experimental results were processed by Pearson's correlation analysis and Principal Component Analysis (PCA). Pearson's correlation analysis and Principal component analysis were used to identify the potential sources (anthropogenic/lithogenic) and distribution of Cu and As which would characterize their interactions between the samples data [10].

RESULTS AND DISCUSSION

Soil characteristics

The soil samples, from the rooting zone of yarrow and soapwort, ranged from extremely acidic (pH = 4.18) to slightly alkaline (pH = 7.54), while the control site M may be estimated as neutral (pH = 6.74-6.85), according to the classification of soil pH recommended by the United States Department of Agriculture [11]. The soil at the site FJ is extremely acidic (pH = 4.18), probably due to the weathering oxidation of pyrite in the soil, which arise from disposal of flotation processes [3]. The overall EC values of the soil samples are relatively low (289-1345 μS/cm) and almost the same as the values in natural soil (200-800 μS/cm), which is necessary for the optimum plant growth [12]. The content of OM in the soil ranged from 3.8% to 23.8%. The soils with the higher values of OM (17.2 and 23.8%) were sampled at the sites S and O which are located in rural area around Bor, on the former agricultural soil.

Comparison of the concentrations

The total concentrations of Cu and As were determined in all the soil samples (Figure 1a). As shown in our previous paper, the soil, from which the samples were taken along with soapwort, is most polluted with Cu, but As is present in high concentrations in the soil of some sites (FJ, BN, O) which are closest to the copper smelter. High concentrations of Cu and As (in almost all the samples) may be a consequence of contamination caused by mining-metallurgical activities that have lasted for more than 100 years in the Bor Region [4].

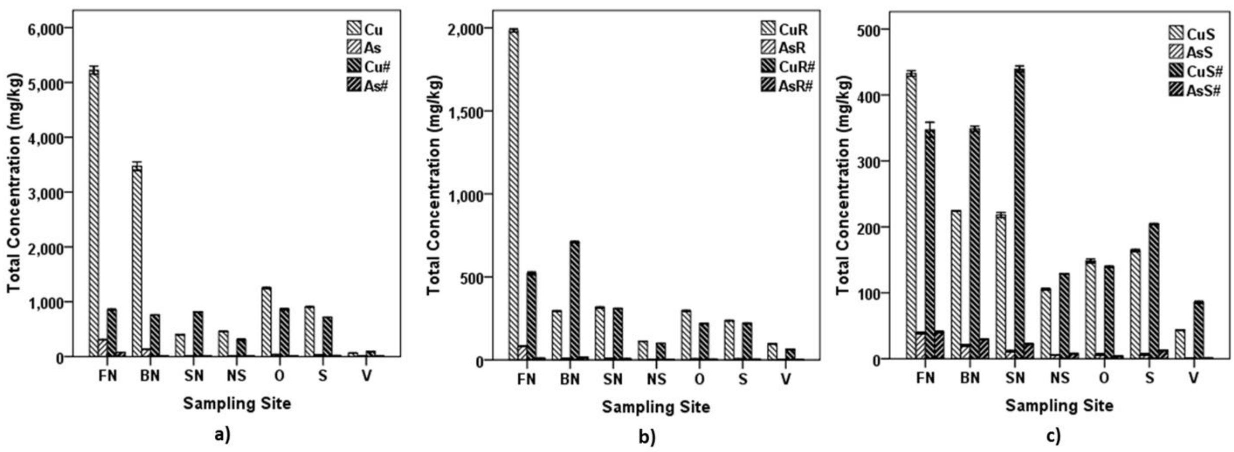

Figure 1 *Comparison of Cu and As concentration in soil (X, X#), root (XR, XR#) and shoot (XS, XS#) of soapwort and yarrow, respectively at various sampling sites. Data are presented as the mean ± standard deviation (SD) for four measurements of the same sample*

More precisely, during the examination of all the sampled soils, the highest total concentrations of Cu and As were recorded in the soapwort soil at the FJ site followed by the site BN, compared to the other sampling sites and all the soil samples of yarrow. However, it should be noted that in the samples of yarrow soil high Cu concentration was recorded at the site O, and high As concentration at the site FJ. Although, both plant species were sampled in relative proximity, there are differences in the content of Cu and As, and at the site SN, a significant deviation from the results of the other samples was observed. At the site SN, twice higher values of Cu and As were recorded in the soil samples of yarrow, compared to the concentrations of the studied elements in the soil of soapwort. Total concentrations of certain elements exceeded the MAC (Cu at 100 mg/kg; As at 25 mg/kg) [13] at the following sampling locations: Cu at the sites FJ, BN, SN, NS, O, and S in the sampled soil of both plants; As at FJ, BN, O and S for the soapwort soil and As at FJ for the yarrow soil. The presented data indicate a high contamination of the examined soil.

The content of Cu and As in parts of yarrow and soapwort sampled from seven sites is given in Figure 1 b, c. The highest content of Cu and As was detected in the root of soapwort from the site FJ: 1984 mg/kg and 80.98 mg/kg, respectively. Increased Cu concentrations recorded in both plant species reflect Cu concentrations in soil, which is a characteristic of a good bioindicator. The contents of Cu in both plants at both urban and rural sites were above phytotoxic concentrations (20-100 mg/kg) [14], except in yarrow root at the site NS and in all the samples at the control site M. On the other hand, phytotoxic concentrations (5-20 mg/kg) [14] of As in soapwort were detected in the root at FJ and in the shoot at FJ and BN. As well, at the sites FJ, BN and SN the content of As exceeded the phytotoxic concentrations only in yarrow shoot. According to the results, a different uptake of Cu and As can be observed in the root and shoot. Thus, a higher Cu concentration was determined in the root of soapwort at all the sites. We can claim the similar observations for yarrow, except for less contaminated sites such as SN, NS and the control site M. Therefore, both plants have a high affinity for Cu and apparently behave as excluders of Cu. By contrast, the content of As in shoot of soapwort was slightly higher compared to root, except for the FJ site, but in yarrow shoot significant (twice) higher concentrations of As were observed in shoot than in root, except at the site M, where the reverse case was recorded. When yarrow has uptaken As in shoot for more than a year in certain amounts, than the results point to the bioaccumulative characteristics of this perennial plant when arsenic is concerned.

Source and influencing factors

Various multivariate techniques such as the PCA and Pearson correlation analysis were also conducted in our previous papers [4,5].

Table 1 *Pearson's correlation matrix of Cu and As in soil, pH, EC, OM, D and different parts of soapwort (N=28)*

	CuR	AsR	CuS	AsS	Cu	As	pH	OM	EC	D
CuR	1									
AsR	**0.997****	1								
CuS	**0.915****	**0.904****	1							
AsS	**0.913****	**0.913****	**0.963****	1						
Cu	**0.843****	**0.840****	**0.883****	**0.952****	1					
As	**0.925****	**0.925****	**0.906****	**0.967****	**0.980****	1				
pH	**-0.537****	**-0.539****	-0.386*	**-0.558****	**-0.660****	**-0.669****	1			
OM	-0.222	-0.237	-0.152	-.0058	0.228	0.077	-.0227	1		
EC	-0.256	-0.212	-0.308	-0.202	-0.183	-0.209	0.108	0.128	1	
D	-0.314	-0.302	**-0.582****	**-0.482****	-0.432*	-0.353	-0.218	-0.124	-0.210	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
XR, XS, X represents the levels of Cu and As in root (R), shoot (S) and soil, respectively.

Table 2 *Pearson's correlation matrix of Cu and As in soil, pH, EC, OM, D and different parts of yarrow (N=28)*

	CuR#	AsR#	CuS#	AsS#	Cu#	As#	pH#	OM#	EC#	D#
CuR#	1									
AsR#	**0.987****	1								
CuS#	**0.737****	**0.678****	1							
AsS#	**0.853****	**0.814****	**0.836****	1						
Cu#	**0.636****	**0.609****	**0.672****	**0.602****	1					
As#	0.428*	0.396*	0.388*	**0.729****	0.448*	1				
pH#	-0.198	-0.216	0.041	-0.365	-0.220	**-0.780****	1			
OM#	-0.405*	-0.408*	-0.342	-0.292	0.167	-0.007	0.048	1		
EC#	0.073	0.029	0.311	**0.554****	0.201	**0.814****	**-0.610****	0.193	1	
D#	**-0.509****	**-0.486****	**-0.555****	**-0.554****	**-0.773****	-0.313	0.204	-0.354	-0.367	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
XR#, XS#, X# represents the levels of Cu and As in root (R), shoot (S) and soil, respectively.

Relationship between concentration of Cu and As in plant parts, soil, physical and chemical parameters of soil and the distance from the source of pollution evaluated by Pearson's correlation coefficients are given in Table 1 and 2. The relations between contents of Cu and As in soil and plant parts of soapwort, and soil pH values (Table 1) show a significant high positive correlation in all the investigated parts, which indicates a similar origin of these elements, i.e. a source of anthropogenic pollution and the same absorption mechanisms in this plant [5,15]. Thus, the negative dependence of Cu and As contents in the shoot, which are correlated with the distance and the pH values, identifies the copper smelter as a major source of pollution via atmospheric deposition. The positive significant correlations of Cu and As in all the samples of yarrow (Table 2) indicate the same origin, except for the correlations of As (As#-AsA#, pH#-As#; EC#-AsA#, EC#-As#, EC#-pH#) in the soil samples and physical and chemical parameters of soil and the correlations obtained between Cu, As and the distance from the smelter. These last correlations suggested a difference between yarrow and soapwort in terms of defense mechanisms, because it was assessed that the yarrow uptakes As through aboveground plant organs, and the sources of this pollution can be individual heating systems or excessive use of rodenticide [16].

Principal component analysis (PCA) was performed to identify and define origin and relationship of Cu and As concentrations in both analyzed plants and the soil (Figure 2). Two components were extracted using varimax rotation and Kaiser criterion. The results show that the obtained components are with eigenvalues >1 which explains 90.4% of total variance in the dataset, with individual contributions of 76.5% and 13.9%. The first factor explained

76.5% of the total variance which was positively loaded with respect to Cu and As mainly for soapwort, while the second factor explained 13.9% of the total variance for Cu and As in yarrow that was also positively loaded. Such results confirm previously obtained conclusions about the different behavior of the investigated plant species under the same environmental conditions. More precisely, soapwort has more affinity for copper which is mostly accumulated in the root, while yarrow uptakes As mainly through the shoot. In any case, both plants represent indicator plant species and factor 1 has the greatest contribution. According to a predominant factor 1, Cu and As are primarily sourced from anthropogenic activities and partially from lithogenic component.

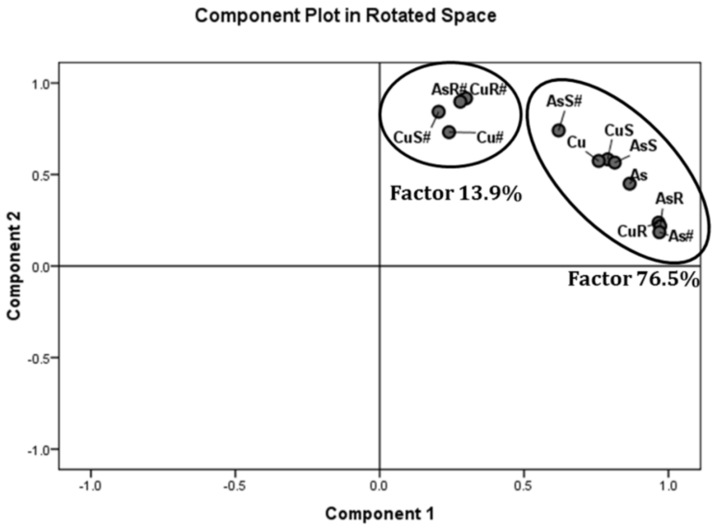

Figure 2 *PCA plot for Cu and As contents in soil and parts of yarrow (#) and soapwort*

CONCLUSION

Based on the data of the compared two investigated plant species, it can be concluded that both of them showed similar accumulation abilities during uptake of Cu, especially in cases of high pollution. It has been observed that increased concentrations of Cu in the soil of both plant species cause reduced translocation to the above-ground parts of plants, indicating their developed defense mechanisms for detoxification and tolerance to high Cu contents and retaining assimilated metals in the root of both plant species. Accordingly, it can be concluded that both plants behave as excluders of Cu. However, in the case of reduced soil contamination by arsenic, both plant species translocate As into shoot, and this is most noticeable for yarrow. Consequently, yarrow can be characterized as a potential bioaccumulator of As. However, both plant species act as excluders of Cu and may be recommended as suitable plants for phytostabilization purposes, regarding the following facts: considerable concentrations of Cu were found in their roots, Cu content was very often over the threshold of phytotoxicity and these plants didn't exhibit visible signs of toxicity. In order to determine these statistically derived conclusions, additional calculations of factors need to be carried out, which can be the subject of further research.

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HAZEL AS A BIOMONITOR OF METAL(LOID) POLLUTION IN THE URBAN AND INDUSTRIAL ZONES OF BOR

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Abstract

The biomonitoring ability of common hazel (Corylus spp.) was assessed at the sampling sites in the urban (U) and industrial (I1, I2, I3) zones of the town of Bor in comparison to the background (B) zone. The content of As, Cr, Cu, Fe, Mn, Ni, Pb and Zn was determined in samples of soil, roots, branches, leaves and catkins. The content of Cu in soil samples exceeded the remediation value at the sites U and I3, while at the sites I1, I2 and B, the limit value was exceeded. In plant samples, the toxic content was noted for Cu in washed leaves at the sites U, I1 and I3. However, biological factors implied low absorption of the metals and metalloids from the soil to hazel roots and leaves, whereby the foliar absorption from the air is possible. In the conditions of anthropogenic pollution in the study area, hazel acted as metal–excluding plant.

Keywords: Air pollution, Biomonitoring, Hazel, Metal(loid), Biological factors

INTRODUCTION

Naturally occurring plant species could be used for determination of: behaviour of plants in real environmental conditions, adaptation of plants to given conditions, as well as the determination of cumulative effect of pollutants in the environment [1]. Plants act as indicators and accumulators of pollutants, which can be useful for the purposes of detection, recognition and monitoring of various substances in the environment. In addition, link between spatial distributions of pollutants with a certain period of time could be made by conducting biomonitoring surveys [2]. Transfer of elements in the soil-plant system is part of the naturally occurring cycles. It represents a very complex process that is conditioned by numerous natural (geochemical, climatic and biological) and anthropogenic factors. Since plants simultaneously respond to elements present in soil and the air, biomonitoring should be carried out simultaneously with soil analysis [3]. Biological factors are successfully used for interpreting the associations between the concentrations of metals and metalloids (metal(loid)s) in the soil, underground and above ground parts of plants, as well for the translocation pathways of metal(loid)s from soil and through the plant itself [4].

The data presented in the paper give the insight of behaviour of hazel in the conditions of high anthropogenic pollution in the Bor area through the analysis of content, accumulation and translocation of metals and metalloids (As, Cr, Cu, Fe, Mn, Ni, Pb and Zn).

MATERIAL AND METHODS

The town of Bor and its surroundings represent suitable area for conducting the biomonitoring studies, since the area is known for pollution originated from anthropogenic sources, of which the copper smelter and the flotation tailing ponds are the dominant ones.

Plant material and soil of broad–leaved deciduous tree *Corylus* spp. (predominantly *Corylus avellana*, common hazel) was sampled in three sampling zones which consisted of five sampling sites, including the background zone. The urban (U) and background (B) zones were represented by one sampling site each, while the industrial zone consisted of three sites (I1, I2 and I3). The position of the sampling sites is given in Figure 1 in regard to the dominant pollution sources.

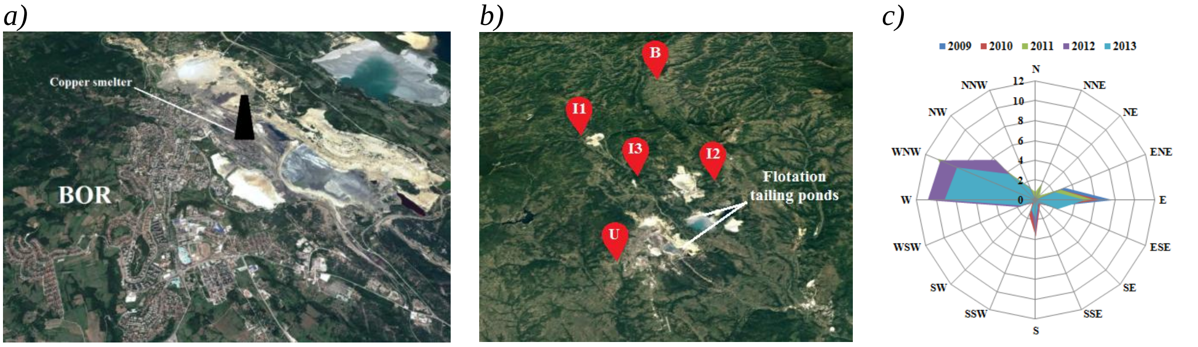

***Figure 1** a) The position of the copper smelter in the town of Bor; b) the sampling sites in the study area of Bor and it's the surroundings with the position of the flotation tailing ponds; c) wind rose diagram for the 5-year period in the study area*

The site I1 was located in the area of the copper mine "Cerovo", 11 km NW from the copper smelter in Bor. The site was characterized with dust emissions from the ore preparation processes and from ore waste hips. The sampling site I2 was located in the area of the copper mine "Veliki Krivelj", 5.5 km N from the smelter; characterized with air pollution from the copper smelter, dust emissions from the ore preparation processes and ore waste hips. The sampling site I3 was in the quarry area, 6 km NNW from the smelter. Dust emissions from exploiting and crushing of limestone were the main air pollution sources at this sampling site. The site U was located in the area located more than 2.5 km SW from the smelter in the town of Bor; characterized with moderate pollution from the traffic and the copper smelter since it was not on the prevailing wind directions (Figure 1c). Rural settlement Gornjane, located 17 km N from the copper smelter, was selected as background due to low air pollution impact [5].

During the sampling, the required common procedures were followed. From each sampling site, samples of soil from the root zone, roots, branches, leaves and catkins were collected with stainless steel equipment and stored into paper bags. The samples from three to five plants per site were mixed into a composite sample. The root and leaf samples were thoroughly washed with distilled water, unlike the branch and catkin samples. Air drying of all material at room temperature was performed prior to grinding to a fine powder. The samples were afterwards digested, according to the EPA method [6], which includes digestion of soil with a mixture of HNO_3 and HCl (1:3) and plant material with a mixture of H_2O_2 and HNO_3 (1:5) in a microwave oven. The element concentrations were obtained by ICP–AES at the Mining and Metallurgy Institute Bor. The element concentrations are expressed as μg g^{-1} of dry weight (dw). Soil pH was determined according to the ISO standard [7], and the content of organic matter (OM) in soil was obtained by the loss-on-ignition method at 450 °C [8]. Biological factor analysis included calculation of Biological Concentration Factor (BCF), Translocation Factor (TF) and Biological Accumulation Coefficient (BAC), according to equations (1)–(3) [5]:

$$BCF=\frac{\text{metal(loid) conc. in roots}}{\text{metal(loid) conc. in soil}} \quad (1)$$

$$TF=\frac{\text{metal(loid) conc. in leaves}}{\text{metal(loid) conc. in roots}} \quad (2)$$

$$BAC=\frac{\text{metal(loid) conc. in leaves}}{\text{metal(loid) conc. in soil}} \quad (3)$$

RESULTS AND DISCUSSION

The data for soil are given in Table 1. The obtained metal(loid) concentrations were compared to the corresponding concentrations from the background site, with the proposed concentrations from the current Regulation concerning the soil pollution, as well as with critical concentrations.

***Table 1** Concentrations of the studied metal(loid)s (µg g^{-1}) in soil*

Site	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH_{H_2O}	OM (%)
U	21.92	32.40	**518.0**	47691	1126.37	18.39	50.38	**200.84**	7.24	7.82
I1	17.09	24.85	**143.64**	38400	876.79	12.25	30.81	97.57	5.91	9.48
I2	**28.91**	62.11	**68.77**	32235	598.98	27.46	29.93	72.57	7.80	5.06
I3	**37.08**	23.15	**418.19**	32739	830.59	11.82	44.50	134.06	7.68	11.39
B	8.40	66.11	**46.14**	29298	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	/	/
Critical[c]	/	50	50	/	/	50	100	300	/	/

[a] LV – limit value [9]; [b] RV – remediation value [9]; [c] critical concentration according to Cicek and Koparal [11]; concentrations exceeding the LVs or RVs shown in bold; / not defined.

The proposed limit values (LVs) for concentrations of metal(loid)s in soil [9] were exceeded for Cu (at all the sites), As (at the site I3, and very close to the LV at the I2) and for Zn (only at the site B). The defined remediation values (RVs) for soil [9] were exceeded only for Cu at the sites U, I1 and I3, which indicated soil alarmingly polluted with Cu. According to the Regulation, in such polluted soils the basic functions are endangered or seriously impaired and therefore remediation, recovery or other measures are required to be implemented [9]. The lowest concentrations of the studied metal(loid)s were detected in the soil samples from the site I2 ("V. Krivelj"), except for the Cu concentration, which was above the LV, but not above the RV. At the background site, the highest concentration was detected for Cr. However, the concentration did not exceed the proposed LV for Cr. At the urban site, the highest content of Cu, Fe, Mn, Pb and Zn in the study area was detected, while at the other two sites in industrial zone (I2 and I3), the content of Ni and As was the highest, respectively. Regarding pH, the results indicated rather neutral reaction of the soil or slightly acidic (at the site I2) [10]. OM showed mostly medium content in soil, from 6% to 20%, except at the site I2 (low content, OM <6%). Generally, this could result in lower availability of metal(loid)s to plants, since the average bioavailability of metal(loid)s is increasing in soils with pH<5. Also, due to bonding of metal(loid)s to OM, bioavailability could be reduced.

In Figure 2 the concentrations of the studied metal(loid)s in hazel parts per sampling sites in the study area are shown. By comparing the obtained concentrations with the suggested ranges from Table 2, it could noticed that only Cu (at the sites U, I1 and I3) and Mn (I3 and B) were contained in toxic concentrations in washed hazel leaves, while the content of other metal(loid)s was in the normal range or between the normal and toxic range. Regarding the content of As and Cu, hazel showed different response to the pollution, since the differences were observed between the urban and industrial sites and the background site.

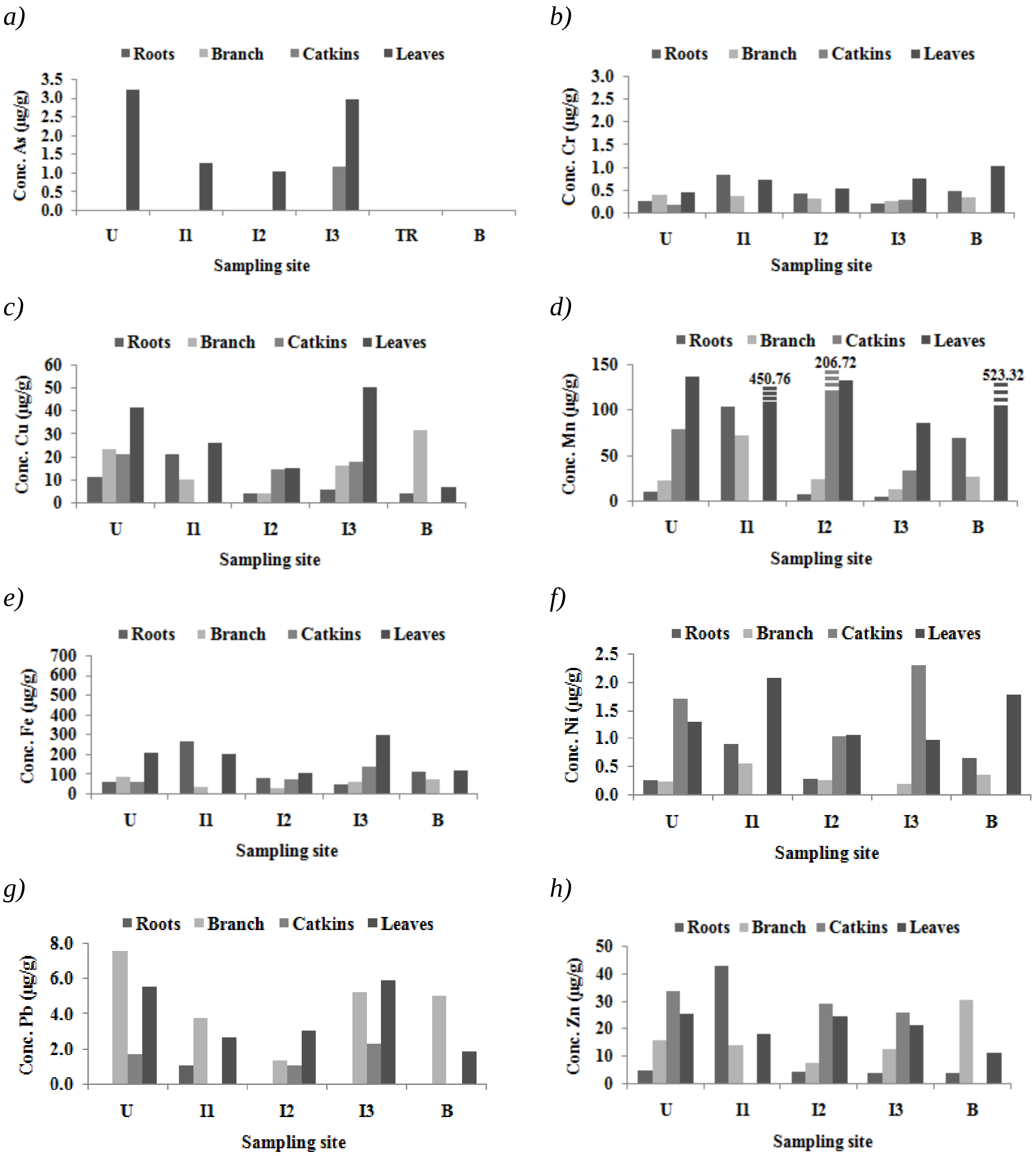

Figure 2 *Concentrations of metal(loid)s (µg g^{-1} dw) in hazel parts (roots, branch, catkins and washed leaves) per sampling site a) As; b) Cr; c) Cu; d) Mn; e) Fe; f) Ni; g) Pb; h) Zn (in the cases of missing bars, concentrations were below the corresponding limit of determination)*

The recommended deficit, normal and toxic concentrations for plants in the literature (Table 2) are based on the wide ranges of concentrations (sometimes overlapping) which are often given for herbaceous plants and fodder [11–13]. Although, not fully relevant for higher plants, these concentrations could indicate how plants reflect the state of the environment.

Tomašević *et al.* [14] and Huseyinova *et al.* [15] published data for traffic–related sites for Turkish (*C. colurna*) and common hazel (*C. avellana*), respectively. However, the data is not comparable with our results, since the concentrations of the studied elements in the published data [14,15] are for unwashed hazel leaves unlike the data given in Figure 2 for washed.

However, in Huseyinova *et al.* [15] contents of Cu, Fe and Zn in washed hazel leaves from a non–polluted site are also given, amounting: 9.1±1.7, 110.2±34.9 and 30.3±7.4 μg g^{-1} dw, respectively. These concentrations are comparable and very similar to the concentrations obtained at the site B in this study (Figure 2c, e and h).

Table 2 *Three ranges of concentrations (μg g^{-1} dw) in mature leaves of plants [11–13]*

Range	As	Cr	Cu	Mn	Fe	Ni	Pb	Zn
Deficit	/	/	2–5	10–30	30–50	/	/	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.

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 metal(loid)s did not accumulate from soil into hazel roots (BCF<<1), probably because of low bioavailable concentrations due to the high OM content and pH value (Table 1).

Table 3 *Biological factors for the studied metal(loid)s*

Factor	Site	As	Cr	Cu	Mn	Fe	Ni	Pb	Zn
BCF	**U**	<0.046	0.008	0.022	0.010	0.001	0.015	<0.020	0.025
	I1	<0.059	0.035	0.149	0.118	0.007	0.074	0.036	0.436
	I2	<0.035	0.007	0.060	0.014	0.003	0.011	<0.033	0.066
	I3	<0.027	0.010	0.014	0.007	0.001	<0.017	<0.022	0.032
	B	<0.119	0.007	0.096	0.088	0.004	0.030	<0.054	0.070
TF	**U**	**>3.227**	**1.782**	**3.711**	**12.348**	**3.314**	**4.612**	**>5.497**	**5.095**
	I1	**>1.268**	0.870	**1.222**	**4.352**	0.757	**2.277**	**2.409**	0.429
	I2	**>1.048**	**1.239**	**3.750**	**15.430**	**1.263**	**3.601**	**>3.037**	**5.103**
	I3	**>2.959**	**3.435**	**8.741**	**15.500**	**6.204**	**>4.842**	**>5.922**	**5.070**
	B	/	**2.155**	**1.630**	**7.561**	**1.020**	**2.716**	**>1.919**	**2.722**
BAC	**U**	0.147	0.014	0.080	0.121	0.004	0.070	0.109	0.126
	I1	0.074	0.030	0.183	0.514	0.005	0.169	0.087	0.187
	I2	0.036	0.009	0.226	0.222	0.003	0.039	0.101	0.336
	I3	0.080	0.033	0.120	0.103	0.009	0.082	0.133	0.161
	B	<0.119	0.016	0.156	0.004	0.662	0.081	0.103	0.191

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 values of BCF did not vary much per sampling sites, except for Mn and Zn in which case slightly higher accumulation was observed at the site I1 (BCF>0.1). Translocation of the studied metal(loid)s from hazel roots to its leaves (TF) occurred almost at all the sites (except for Cr, Fe and Zn at the site I1). It seems that all the accumulated quantity of the metal(loid)s from soil into roots (although small according to BCF), were translocated to hazel leaves. According to the BAC values, the direct influence of soil metal(loid) concentrations to corresponding content in the leaves was not observed since the intensity of uptaking elements into leaves from soil was in the range of a week absorption (0.01–0.1) [16]. However, in the case of Cu, Mn, Pb and Zn, at almost all the sampling sites, moderate absorption (0.1–1) was observed [16]. According to Baker [17], who was among the first authors who defined accumulation, indication and exclusion strategies of plant, the values BAC<1 indicated exclusion abilities of hazel in the given conditions.

CONCLUSION

The biomonitoring ability of hazel was assessed at the sampling sites which were characterised with different level of air pollution due to position of the dominant sources of pollution (i.e. copper smelter, flotation tailing ponds, two copper mines and quarry) in the Bor area. The concentrations of the analysed metal(loid)s showed influence of mining–metallurgical operations on the content of As and Cu in the soil, since the Cu concentrations exceeded the corresponding limit, and in two cases, the remediation values for soils. The results of biological factors indicated that foliar concentrations of the metal(loid)s were not influenced by the corresponding soil content, whereas foliar absorption could be considered. Based on the classification of plants as indicators, accumulators or excluders, it seems that hazel acted as metal–excluding plant in the polluted environment of Bor and it's the surroundings.

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BIOINDICATION OF SOIL POLLUTION WITH Cu, Zn AND As BY ROOTS OF PLANTS

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Abstract

Plants growing on soils enriched with metals and metalloids are usually genetically tolerant to high concentrations, and have excellent adaptation abilities to extreme environmental conditions. That fact in combination with the extreme soil pollution in the town of Bor and the surroundings, gave a good basis for the environmental research. Assessment of pine, linden and elder roots ability to indicate soil enrichment with Cu, Zn and As was conducted. Samples were colected at the sites seleceted in regard to the vicinity of the copper smelter, flotation tailing ponds, overburden dumps and open pits. It was observed that linden and elder, unlike pine roots, had ablity to indicate soil enrichment with Cu, Zn and As, which was the most obvious at the sites with the highest metal/metalloid contents. On the other hand, pine roots have developed the mechanisms for resistance to As accumulation in the roots, especially in the conditions of high As soil content.

Keywords: Copper, Zinc, Arsenic, Bioindication, Soil, Root

INTRODUCTION

Roots of plants are in constant interaction with the polluting substances in soil [1]. Retention of such substances in roots could be used for bioindication of soil pollution. One more advantage of such interaction may be that plants growing on naturally metal–enriched soils tend to be genetically tolerant to high metal concentrations, having excellent adaptation abilities to extreme environmental conditions, thus having the potential for phytoremediation [2,3]. The soil of the town of Bor and the surroundings was well known for the extreme pollution with numerous metals and metalloids [4,5]. Such state of the environment was good basis for the examination of pine, linden and elder roots ability to indicate soil pollution with Cu, Zn and As.

MATERIALS AND METHODS

Sampling of soil and roots was conducted during 2013, before the new smelter and sulphuric acid plant started working. That ensured the information about the state of the biota in the extreeme environmental conditions. Plant species (pine, linden and elder) with developed root system which could indicate potential long term bioacumulation of polluted substances from the soil, as well as, developed adaptation abilities, were selected. From the scientific standpoint of view, selected species were insufficiently or even not examined at the given aspect. Detail soil sampling and preparation was given in the paper by Kalinovic *et al*. [4]. Root samples were collected from 7 zones/10 sampling sites (Figure 1): urban-industrial

(UI), urban (U), suburban (SU), industrial (I1-surroundings of the Copper Mine Veliki Krivelj and I2-surroundings of the Copper Mine Cerovo), tourist (T1-Brestovac spa and T2-Bor lake), rural (R1-village Oštrelj and R2-village Slatina) and background (B-village Gornjane). Roots (10–20 cm depth, thickness up to 4 cm) of three to five plants of each plant species were sampled, at each of the sampling sites. Composite root sample of each plant species per sampling site were formed. After removing of soil particles, washing with destiled water and air drying at the room temperature, root samples were ground to a fine powder and stored at room temperature until analysis. Samples were digested according to the U.S. EPA method 3050B [6], and concentrations (μg/g dry mass) of Cu, Zn and As in extracts were determined by ICP–AES at the Institute of Mining and Metallurgy Bor (Serbia). The values of the Enrichment Factor (EF) were calculated by dividing the concentration of a certain element in soil/roots from the polluted sampling site and the concentration of the corresponding element in the soil/roots from the background sampling site. The values of EF>2 indicated enrichment.

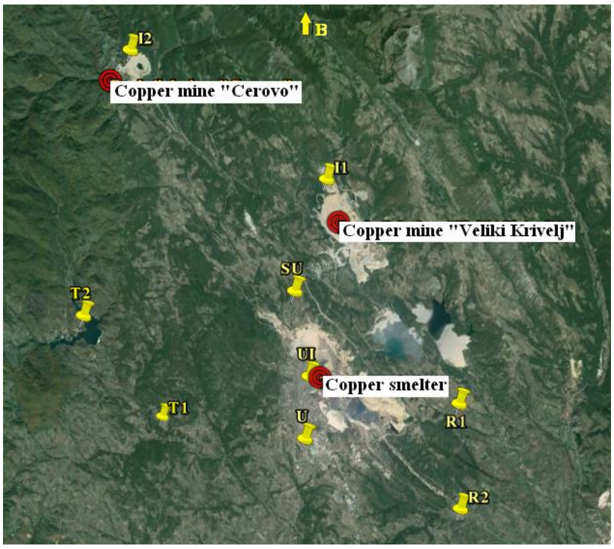

Figure 1 *Map of the study area in the town of Bor and the surroundings*

RESULTS AND DISCUSSION

Data about pollution of soil from the selected sampling sites (Figures 2a, 3a, 4a, Tables 1-3) were thoroughly discussed earlier in the papers by Kalinovic *et al*. [4,7], serving here as support for the analysis. The Cu and As soil concentrations were above the maximum allowable concentrations (MAC) [8] at almost all the the sampling sites. It was observed that soil was less polluted with Zn. Hovewer, the highest exceedances of the MAC [8] for Cu, Zn and As were in the urban-industrial zone. Since aerial parts of plants are surrounded with air and could be used for the indication of air pollution [4,5], it was assumed that roots of plants could indicate the pollution of root surrounding media that is soil. Such aspect was used in the following discussion.

Copper

The highest Cu concentrations in pine, linden and elder soil were obtained in the samples from the UI site, following the order pine<linden<elder (Figure 2a). According to that, Cu concentrations in the roots of the examined plants sampled from the same site were expected to be higher than in the roots from the rest of the sites. However, such assumption was not proved correct. Only linden roots had the highest contents in the UI site, while such regularity

was not observed for pine and elder. It is interesting that Cu content in the pine roots from the B site was higher than in the samples of roots from the rest of the sites (Figure 2b). Pine roots were not enriched with Cu at any of the sampling sites (EF<2) (Table 1), but EFs for Cu in soil were >2 at all the sampling sites. Because of that, it can be said that pine roots are not suitable for determination the soil enrichment with copper. The values of EFs for Cu in linden and elder roots were significantly ≥2 for samples from almost all the sampling sites, except at the I2 for linden and T1 and I1 for elder roots. Also, the EF values for Cu in soil samples of linden and elder were >2 at all the sampling sites. According to that, linden and elder roots seems to have the ability to indicate soil enrichment with Cu.

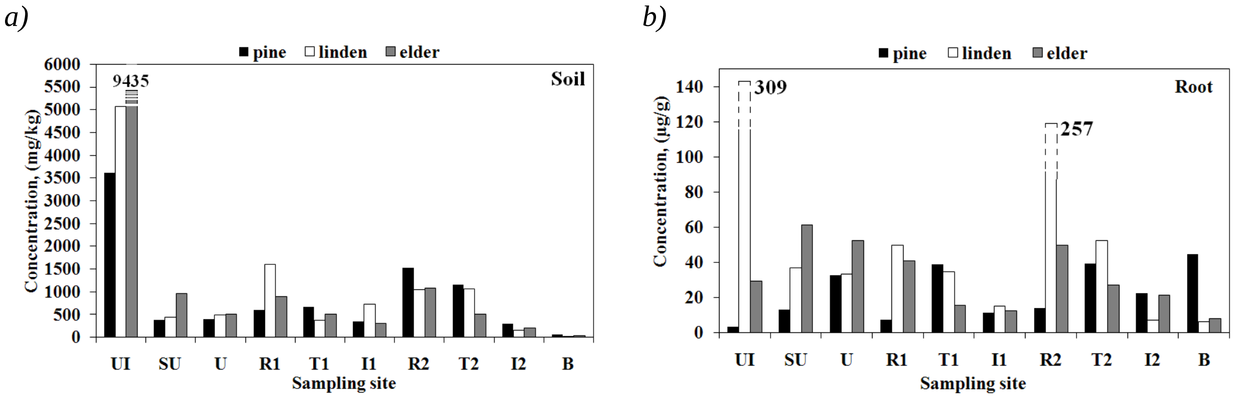

Figure 2 *Concentrations of Cu in a) soil and b) roots of pine, linden and elder depending of the sampling site*

Table 1 *Enrichment Factor values of Cu in soil and roots of pine, linden and elder*

Plant species	pine		linden		elder	
Sampling site	**soil**	**root**	**soil**	**root**	**soil**	**root**
UI	53.33	0.08	223.12	50.74	239.37	3.72
SU	5.61	0.29	19.54	6.07	24.32	7.79
U	5.81	0.73	21.95	5.43	12.81	6.65
R1	8.88	0.17	70.29	8.18	22.82	5.21
T1	9.76	0.88	16.49	5.66	12.98	1.98
I1	5.09	0.26	31.70	2.50	7.56	1.57
R2	22.45	0.32	46.20	42.18	27.58	6.31
T2	17.03	0.89	46.67	8.64	12.89	3.46
I2	4.40	0.50	6.80	1.19	5.12	2.72

Obtained results suggested the potential different Cu uptake and retention mechanism of the roots of plants in the conditions of the extreme soil pollution with this element. The critical Cu concentration for the roots of pine seedlings determined by Fuentes *et al*. [9] was not exceeded in any pine root samples from the study area. Copper concentration in the pine roots from the vicinity of the Cu-Ni smelter [10], amounted 593 μg/g, was much higher than Cu contents of the pine roots from the Bor and the surroundings.

Zinc

The highest Zn concentrations in the pine, linden and elder soil were in the samples from the UI site, following the order pine<linden<elder, as in the case of Cu (Figure 3a). According to the results (Figure 3b), neither of the examined plant species did not stand out by the highest Zn roots concentration compared with other two species, considering all the sampling sites. The highest concentrations of Zn in linden and elder roots (elder<linden) were

determined in the samples from the UI site, while the highest Zn concentrations in the pine roots were determined in the samples from the B site, as in the case of Cu. Zn contents in pine roots from the UI site were lower than Zn concentrations in the pine roots from the vicinity of the Cu-Ni smelter [10].

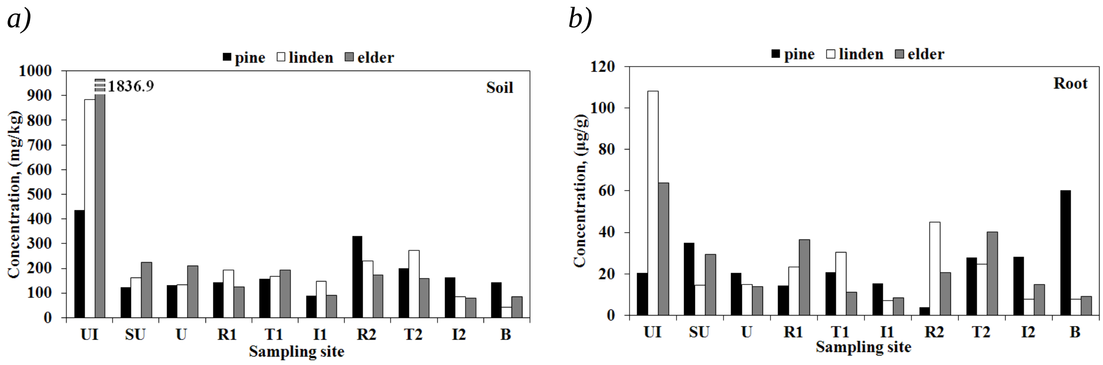

Figure 3 *Concentrations of Zn in a) soil and b) roots of pine, linden and elder depending of the sampling site*

None of the EF values for the pine roots were >2, even at the UI and R2 sites where EFs for the pine soil were >2 (Table 2). The values of EF for linden and elder roots from a couple sampling sites indicated the enrichment with Zn, with the highest values for the UI site. It is significant to highlight that EF values for linden and elder roots were >2, for the samples from the UI and R2 sites, where the soil samples of these plants were enriched with Zn, too. The Zn contents in the soil from these sampling sites were one of the highest, compared to the rest. These results indicated that linden and elder roots might have the ability to indicate soil pollution with Zn, but only at certain contents of this element in soil.

Table 2 *Enrichment Factor values of Zn in soil and roots of pine, linden and elder*

Plant species	pine		linden		elder	
Sampling site	**soil**	**root**	**soil**	**root**	**soil**	**root**
UI	3.07	0.34	21.70	14.05	21.81	7.12
SU	0.87	0.58	3.95	1.88	2.67	3.28
U	0.93	0.34	3.23	1.93	2.49	1.54
R1	1.01	0.23	4.71	3.03	1.48	4.04
T1	1.10	0.34	4.07	3.97	2.27	1.24
I1	0.62	0.25	3.62	0.93	1.08	0.93
R2	2.34	0.06	5.58	5.86	2.06	2.28
T2	1.41	0.46	6.68	3.21	1.87	4.47
I2	1.15	0.47	2.06	0.99	0.94	1.66

Arsenic

Arsenic contents in soil samples of all of the three plant species from the UI site were much higher than the concentrations in the soil samples from the rest of the sites (Figure 4a). Such regularity was observed only for As content of linden roots from the UI site compared with the As content of the linden roots from the rest of the sampling sites (Figure 4b). Only As contents of the pine roots from the T1 and B sites, were higher than the lower limit of determination. These concentrations were at same time higher than the rest of the As contents of the root samples of the examined plant species. The arsenic concentrations in pine soil from the T1 and B sites were not the highest. Such results indicated that As contents of pine roots were not only depended by total As concentrations in soil of the root zone. It could be said that pine roots have developed the natural restriction mechanisms for the As accumulation in the roots, especially in the conditions of high As soil contents.

a) *b)*

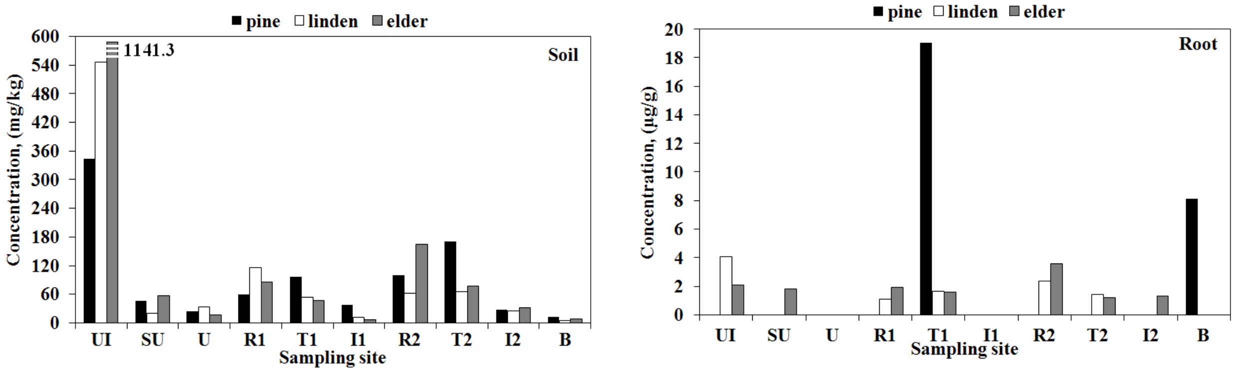

Figure 4 *Concentrations of As in a) soil and b) roots of pine, linden and elder depending of the sampling site. Bars are missing in the case of concentration below the lower limit of determination (<1 µg/g)*

Enrichment of pine roots with As was observed only for the T1 site (Table 3), which was not enough for discussion about its ability to indicate the soil pollution with As. The values of EF for As in linden and elder roots were for sure >2, only for the samples from the UI and R2 sites. The EF values for As in linden and elder soil samples from the mentioned sites were the highest and >2 as well, which indicated that linden and elder roots could be used for indication of soil pollution with As.

Table 3 *Enrichment Factor values of As in soil and roots of pine, linden and elder*

Plant species	pine		linden		elder	
Sampling site	**soil**	**root**	**soil**	**root**	**soil**	**root**
UI	**29.07**	<0.12[a]	**107.26**	**>4.07[b]**	**154.50**	**>2.12[b]**
SU	**3.95**	<0.12[a]	**3.94**	/[c]	**7.80**	>1.82[b]
U	1.98	<0.12[a]	**6.49**	/[c]	**2.16**	/[c]
R1	**4.97**	<0.12[a]	**22.70**	>1.09[b]	**11.67**	>1.93[b]
T1	**8.14**	**2.34**	**10.59**	>1.65[b]	**6.25**	>1.61[b]
I1	**3.16**	<0.12[a]	**2.28**	/[c]	0.97	/[c]
R2	**8.36**	<0.12[a]	**12.17**	**>2.40[b]**	**22.30**	**>3.61[b]**
T2	**14.39**	<0.12[a]	**12.87**	>1.46[b]	**10.49**	>1.23[b]
I2	**2.26**	<0.12[a]	**4.83**	/[c]	**4.25**	>1.32[b]

[a] values obtained by dividing the lower limit of determination by the concentration in roots from the B site; [b] values obtained by dividing the roots concentration from the certain sampling site by the lower limit of determination; [c] concentrations in roots from the certain sampling site and background site were below the lower limit of determination.

Pine roots from the tailing of the old Sb mine contained higher As concentrations than the pine roots sampled in the vicinity of the copper smelter and overburden dumps in the town of Bor and the surroundings [11].

CONCLUSION

From the given aspect of the analysis it could be concluded that soil and root Enrichment Factor values of Cu, Zn and As in combination with the obtained concentrations gave good direction during the data analysis. It has been showed that neither of the examined plant species was stand out by the highest accumulation ability of Cu, Zn or As in their roots, considering all the examined sampling sites. It has been proven that examined species acquire different uptake and retention mechanism in the conditions of the extreme soil pollution. At the most polluted area of the town of Bor (the UI site) and the surroundings, concentrations of the examined elements in roots were increasing according to the series pine>elder>linden. Linden and elder roots have the ability to indicate soil enrichment with Cu, unlike pine roots. The results suggested the potential different Cu uptake and retention mechanism of the roots of plants in the conditions of the extreme soil pollution with this element. Linden and elder roots might have the ability to indicate soil pollution with Zn, but only at enough high contents of this element in soil. Arsenic contents of pine roots did not depended only by total As concentrations in the soil root zone. It could be said that pine roots have developed the natural mechanisms to resist to the As accumulation in the roots, especially in the conditions of high As soil contents. Linden and elder roots could be used for indication of soil pollution with As. Total Cu, Zn and As concentrations in soil and roots from the town of Bor and the surroundings were good basis for the assessment of pine linden and elder roots ability to indicate soil enrichment with these elements.

ACKNOWLEDGEMENT

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CONTENT OF Ni AND Mo IN SOIL AND PLANT PARTS OF WILD ROSE (*Rosa* spp.) IN BOR (SERBIA)

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Abstract

The aim of this study was to assess the content of Ni and Mo in the root zone soil and parts of wild rose (Rosa spp., predominantly Rosa canina L.), sampled from fourteen sampling sites in Bor and its surroundings. The maximum concentrations of Ni and Mo in root zone soil was found in samples from the sites in the close vicinity of the mining-metallurgical complex or in the prevailing wind direction. Higher Ni concentrations in samples from the background site in regard to the other sampling sites indicated the natural presence of Ni in the soil around this site. The content of Mo in soil samples exceeded the limit value at five sampling sites. The highest concentration of Ni in the parts of wild rose (roots, branches, leaves, fruits) was found in the samples from I3, I2, R2 and R1 sites, while for Mo was found in the samples from UI, R2 and R1 sites. According to calculated biological factors it can be noted that wild rose excluded Ni and Mo from the soil. Also, based on the values of bioconcentration and translocation factor it can be concluded that wild rose is not suitable for phytoextraction and phytostabilization.

Keywords: Environmental pollution, Wild rose, *Rosa* spp., Biological factors

INTRODUCTION

Industrial and traffic emissions, usage of metal-containing agricultural products and other anthropogenic processes are the main sources of potentially toxic elements into the environment [1,2]. Mining activities also generate huge amounts of waste. Uptake and accumulation of elements in large quantities by crop or plants growing in mining areas represent the major pathway for their entrance into the food chain [3]. Some elements in the environment pose a significant risk to the quality of soils, plants, waters and humans [4].

Usage of herbs and medicinal plants to relieve and treat many human diseases is increasing all over the world. It is important to have a good quality control for herbs and plant in order to protect consumers from the contamination [5]. Fruit of wild rose (rosehips) contains minerals and vitamins (A, B3, C, D and E), while other organs of the plant comprise tannin organic substances, which have medicinal properties [4]. The fruits are commonly used to make jam, marmalade, fruit juice etc., while the dried fruits and roots are excellent for making tea [6].

The aim of this study was to assess the content of Ni and Mo in the soil and parts of wild rose (roots, branches, leaves and fruits), sampled from fourteen sampling sites in Bor and its surroundings, with different pollution level. Also, biological factors were calculated indicating possibilities of use wild rose in phytoremediation purposes.

MATERIAL AND METHODS

The study area was town of Bor and its surroundings, located in the central part of the Eastern Serbia. The copper smelter, which is a part of the mining-metallurgical complex (MMC), is the primary air pollution source, while the open pits (Cerovo and Veliki Krivelj), ore waste heaps and flotation tailing ponds represent secondary air pollution sources [7,8].

Naturally present deciduous shrub wild rose (*Rosa* spp., predominantly *Rosa canina* L.) was selected for analysis. Plant material and soil samples were collected from fourteen sampling sites during 2013. Description and position of the sampling site in regard to the pollution sources, as well as wind rose diagram are given in Table 1 and Figure 1. Sampling site B was characterised as a background site since it was not under the direct impact of pollution from the MMC, because it is physically protected by mountain massifs.

Table 1 *Description of sampling sites and the dominant wind directions*

Sampling site	Location	Wind direction
B	Rural settlement Gornjane, 17 km N from the copper smelter.	S
TR	The local traffic road, 20 km SSW from the copper smelter.	N, NNE
T1	Brestovac spa, 4.5 km WSW from the copper smelter.	ENE, E
T2	Bor lake, 7 km WNW from the copper smelter.	ESE, E
I1	The surroundings the quarry, 6 km NNW from the copper smelter.	SSE, SE
I2, I3	The surroundings of the copper mine Cerovo, 11 km NW of the copper smelter.	SE
I4	The surroundings of the copper mine Veliki Krivelj, 5.5 km N from the copper smelter.	S
I5	The surroundings of the flotation tailing ponds of the copper mine Veliki Krivelj, 3 km NE from the copper smelter.	SW
UI	Town of Bor, 0.5–2.5 km SW from the copper smelter.	ENE, NE
U	Town of Bor, >2.5 km SW from the copper smelter.	ENE, NE
SU	Suburban site Brezonik, 2.5 km NW from the copper smelter.	SE, ESE
R1	Rural settlement Oštrelj, 4.5 km ESE from the copper smelter.	WNW, WN
R2	Rural settlement Slatina, 6.5 km SE from the copper smelter.	WNW, WN

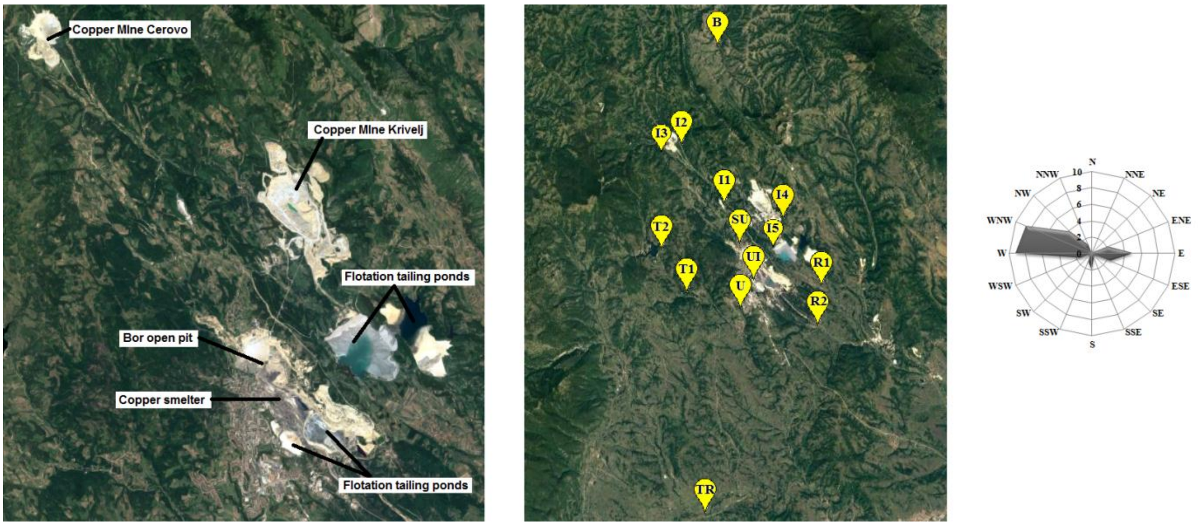

Figure 1 *The position of pollution sources, the sampling sites of soil and parts of wild rose, and wind rose diagram (%) for 2013*

Parts of wild rose (leaves, branches, fruits, roots) and root zone soil, were collected from the three to five shrubs at each site and combined into composite sample per site. The root and one half of leaf samples were washed with distilled water. Prior to analysis, all samples were air dried at room temperature and then were grounded to a fine powder. All plant and soil samples were digested according to the U.S. EPA method 3050B [9]. The chemical analyses were determined by ICP–AES at the Mining and Metallurgy Institute Bor.

RESULTS AND DISCUSSION

Descriptive analysis of Ni and Mo in root zone soil and plant parts (roots, branches, leaves and fruits), as well as soil pH values are shown in Table 2. In the study area, soil pH ranges from 4.37 to 7.82.

Table 2 *Descriptive analysis of soil pH and concentration (mg/kg) of Ni and Mo in root zone soil and plant parts*

Element		N	Range	Minimum	Maximum	Mean	Std. deviation
	pH	14	3.45	4.37	7.82	6.38	1.06
Ni	**Soil**	14	38.01	5.24	43.25	16.12	9.15
	Roots	14	2.62	0.41	3.03	1.10	0.71
	Branches	14	0.82	0.28	1.10	0.68	0.27
	Washed leaves	14	1.83	0.53	2.36	1.32	0.52
	Unwashed leaves	14	4.54	0.43	4.97	1.47	1.16
	Fruits	14	1.43	0.23	1.66	0.63	0.41
Mo	**Soil**	14	54.09	0.91	55.00	6.13	14.16
	Roots	2	2.76	0.30	3.06	1.6805	1.95
	Branches	2	0.01	0.25	0.26	0.25	0.01
	Washed leaves	12	1.67	0.40	2.07	0.74	0.48
	Unwashed leaves	12	3.26	0.32	3.57	1.03	0.87

The concentrations of Ni and Mo in root zone soil at the 14 sampling sites in Bor and its surroundings are shown in Figure 2. Maximum Ni concentration in soil was found at the U site. This concentration was above limit value, which amount 35 mg/kg according to the Serbian Regulation [10]. Sampling site U was in the close vicinity of the mining-metallurgical complex (MMC) which could affect the higher concentrations of Ni. Although the B site was characterized as the background, higher Ni concentrations in regard to the other sampling sites indicated the natural presence of Ni in the soil and rocks around this site. Minimum Ni concentration was found at the sites I1 and UI.

The concentrations of Mo in the soil exceeded the LV (3 mg/kg) proposed by the Serbian Regulation [10] at the U, R2, R1, I5 and UI sampling sites. The U, UI and I5 sites were in the close vicinity of the pollution sources, while the WNW and WN winds influenced the distribution of pollution from the MMC towards the R1 and R2 sites.

Enrichment factor (EF) was used to determine the amount of metals introduced from anthropogenic sources into the soil. EF represents the ratio of metal concentration in the soil sample and its concentration in background soil sample [3]. The EF values for Ni and Mo in the soil are shown in Figure 3. The calculated EF values for Ni indicated the absence of enrichment at 13 sampling sites, which suggested its mostly natural origin in the soil. Only at the U site moderate enrichment with Ni was noted. The enrichment of soil with Mo ranged from non-enriched to extremely highly enriched. Moderate enrichment with Mo was found at the UI, R1 and I5, but still reaching very high enrichment with Mo at the U site, significant enrichment at the R2 site and reaching extremely enrichment at the U site, indicating anthropogenic input of Mo into the soil.

a) b)

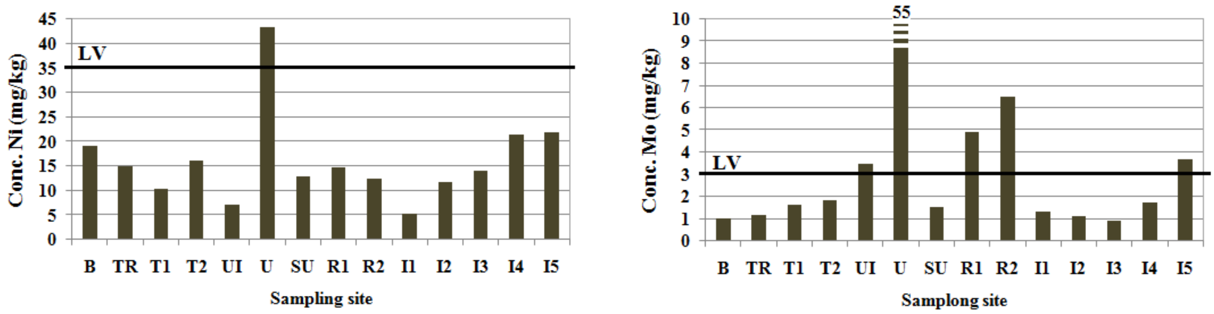

Figure 2 *Concentrations of a) Ni and b) Mo in root zone soil of wild rose at the 14 sampling sites (solid lines represent the LV according to the Serbian Regulation [10])*

a) b)

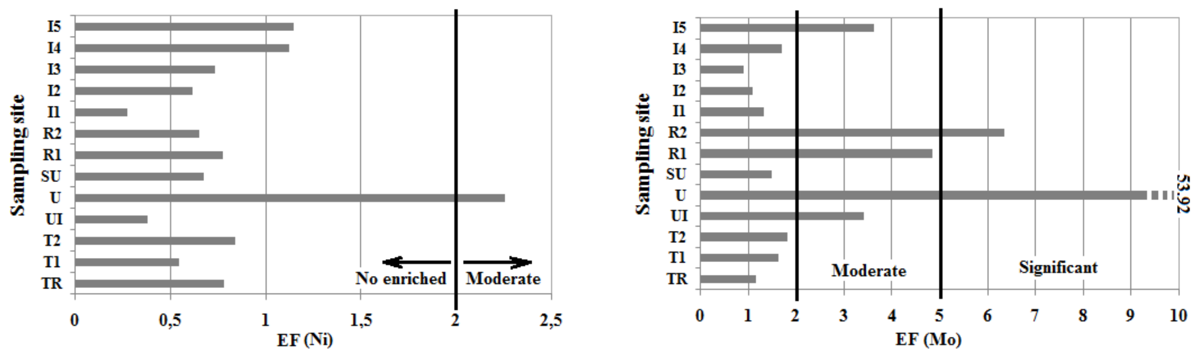

Figure 3 *Enrichment Factor of a) Ni; b) Mo, for the root zone soil of wild rose*

The concentrations of Ni and Mo in plant parts of wild rose at the 14 sampling sites in Bor and its surroundings are shown in Figure 4a and b, respectively. Based on the obtained results, the highest concentration of Ni in the plant parts was found in the samples from I3, I2, R2 and R1 sites. Sites I3 and I2 were located in the vicinity of the copper mine Cerovo, while the sites R2 and R1 were on the WNW and WN winds directions. The concentrations of Mo were below the limit of determination (LD) in the root and in the branch samples from twelve sampling sites, in washed leaf and in the unwashed leaf samples from two and in the fruit samples from all the sampling sites. It can be noted that the highest concentration of Mo in the parts of wild rose was found in the samples from UI, R2 and R1 sites. Site UI were in the close vicinity of the copper smelter, while the dominant winds influenced the distribution of pollution towards the R1 and R2 sites. Vural [4] in his study determined the ranging values from 0.50 to 3.50 mg/kg for Ni and 0.17 to 2.34 mg/kg for Mo in the leaves of wild rose, respectively. The content of Ni and Mo in the leaf samples were higher or in the range of our results. According to Stefanut *et al.* [11] content of Ni in the fruits was higher than in our study.

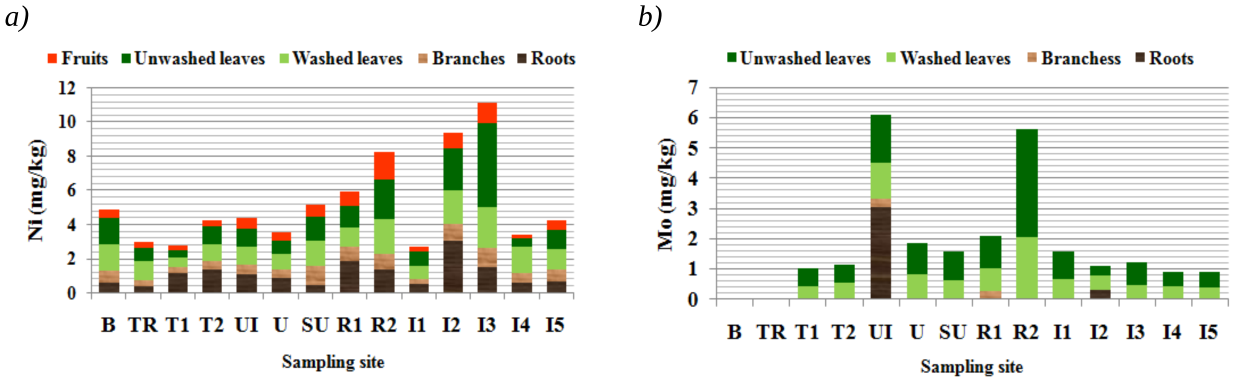

Figure 4 *Concentrations (mg/kg) of a) Ni; b) Mo in parts of wild rose*

Biological factor analysis

Biological factor analysis included calculation of Biological Accumulation Coefficient (BAC), Bioconcentration Factor (BCF) and Translocation Factor (TF). BAC is defined as the ratio of metal concentration in washed leaves to its concentration in soil, indicating plant ability to absorb elements from soil [12]. In order to assess the metal accumulation efficiency in plant, the BCF and the TF were calculated. BCF was defined as the ratio of metal concentration in the roots to that in the soil, while TF represented the ratio of metal concentration in the washed leaves to its concentration in the roots [3]. According to Christou [3] plants with both BCF and TF >1 have the potential to be used in phytoextraction, whereas plants with BCF >1 and TF <1 have the potential to be used for phytostabilization. The values of the biological factors are shown in Table 3.

Table 3 *Bioconcentration Factor (BCF), Biological Absorption Coefficient (BAC) and Translocation Factor (TF) for wild rose*

	Factor	BAC		BCF		TF	
	Element	Ni	Mo	Ni	Mo	Ni	Mo
Sampling site	**B**	0.08	<0.29	0.03	<0.16	**2.58**	-
	TR	0.07	<0.25	0.03	<0.27	**2.73**	-
	T1	0.05	0.27	0.11	<0.09	0.47	**>1.48**
	T2	0.06	0.28	0.08	<0.29	0.73	**>1.77**
	UI	0.15	0.35	0.15	**1.85**	***0.98***	0.39
	U	0.02	0.01	0.02	<0.05	**1.03**	**>2.78**
	SU	0.11	0.42	0.03	<0.06	**3.27**	**>2.14**
	R1	0.07	0.15	0.12	<0.20	0.61	**>2.49**
	R2	0.16	0.32	0.11	<0.01	**1.48**	**>6.91**
	I1	0.14	0.49	0.1	0.33	**1.36**	**>2.21**
	I2	0.17	0.44	0.26	<0.25	0.65	**1.61**
	I3	0.17	0.52	0.11	<0.22	**1.54**	**>1.58**
	I4	0.07	0.24	0.03	<0.08	**2.42**	**>1.4**
	I5	0.05	0.11	0.02	<0.17	**1.78**	**>1.33**

The values given in bold represent BCF >1 and TF >1; the values given in bold and italics represent TF ≈ 1; '-' both values are missing for the calculation; the values with '<' or '>'are obtained by replacing the missing element concentration with the LD of the element in the leaf/root samples (the LD for Mo 0.3 mg/kg).

BAC values for Ni and Mo were <1, which indicated that wild rose excluded this elements in existing conditions [13]. The calculated BCF values for the Ni and Mo were <1, except for Mo at the UI site, indicating that there were not effective accumulation of the metals from soil to roots. The TF values for Ni and Mo in most cases were >1, so it can be assumed that wild rose effectively translocated the elements from the roots to the leaves. However, based on the BCF and TF values it can be said that wild rose is not useful for phytoextraction and phytostabilization.

CONCLUSION

In this study, were determined Ni and Mo in soil and wild rose samples from Bor and its surroundings (Serbia). The highest concentrations of Ni in the soil were found at the sites which were in the close vicinity of the MMC. However, higher Ni concentrations from B site in regard to the other sampling sites indicated the natural presence of Ni in the soil in the surrounding of mountain massifs. The concentrations of Mo in the soil exceeded the LV at five sites indicated soil contamination with this element. Also, the highest concentrations of the Ni and Mo in the parts of wild rose were found in the samples from the sites which were in the vicinity of pollution sources (copper smelter, copper mine) or in the prevailing wind directions. Based on obtained results it can be concluded that content of elements in plants depend on the anthropogenic activities and geochemical characteristics of the soil, as well as the ability of plants to accumulate these elements. So, it is important to have a good quality control for plants which are used in therapeutics purposes in order to protect consumers from toxic elements.

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THE EFFECT OF CONTAMINATION WITH PETROLEUM-DERIVED SUBSTANCES ON SOIL MITE COMMUNITIES AND SOIL ENZYMES ACTIVITY

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Abstract

The aim of this study was to determine the impact of various petroleum-derived substances, namely petrol, diesel fuel and spent engine oil on the soil mite communities and enzymes activity. The soil surface was contaminated with petrol, diesel fuel and engine oil, at 6,000 mg kg^{-1} d.m., with and without ZB-01 biopreparation. The results show that species composition of Mesostigmata depends on the type of petroleum-derived substances. The applied bioremediation did not affect the mite community. Pearson's correlation coefficient was used to analyze the relation between environmental variables and total abundance of Mesostigmata and Oribatida. Total abundance of Mesostigmata showed a statistically significant negative correlation with fluorescein diacetate (FDA) hydrolysis. Canonical correspondence analysis (CCA) indicated that Zn, Cd, Pb, Cu and N content and soil moisture and pH were the most important variables for the species composition of Mesostigmata. Principal component analysis (PCA) and Pearson's correlation coefficient showed an effect of bioremediation on the activity of acid phosphatase and dehydrogenase in soil contaminated with engine oil, i.e. enzyme activity depended on the type of contamination. Redundancy analysis (RDA) showed a statistically significant relationship between enzyme activity and the relationship between enzyme activity and the levels of Zn, N and C.

Keywords: Soil pollution, Petroleum-derived substances, Soil mite communities, Soil enyzme activity

ECO-INDUSTRIAL SYMBIOSIS AS A MODEL OF MANAGEMENT OF INDUSTRIAL AREAS

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Abstract

Industrial ecology is a new approach to the industrial design of products and processes and the implementation of sustainable manufacturing strategies. It is a concept in which an industrial system is viewed not in isolation from its surrounding systems but in concert with them. Industrial ecology seeks to optimize the total materials cycle from virgn material to finished material, to component, to product, to waste product, and to ultimate disposal. Environmentally friendly symbiosis between diverse local or regional businesses should become valuable component of modern industrial development. Industrial symbiosis, as part of the emerging field of industrial ecology, demands resolute attention to the flow of material and energy through local and regional economies. This article reviews the efforts of developing industrial symbiosis networks. The paper introduces a case study on the production of phosphoric acid and the usage of derived by-products. This is the example of the implementation of the eco-industrial symbiosis model in practice, aimed to reduce the consumption of natural resources.

Keywords: Industrial ecology, Eco-industrial symbiosis, Production of phosphoric acid, By-products

INTRODUCTION

In industrial systems, there is a tendency to emphasize the interdependence between enterprises. A unified management system has become a widely recognized approach. Companies/ enterprises become an integral part of chains or networks of suppliers and consumers, similar to the chains and networks encountered in autochthonous ecosystems. With the aim to ensure their productivity, industries depend upon the resources found in the environment, while individual enterprises and corporations become parts of a unique system, they depend upon one another and co-operate in order to remain on the market [1].

Successful industrial systems are based on the study of mass and energy trends, which contributes to the minimization of quantities of waste materials [2]. An important feature of the technological system, which is considered as a part of the industrial system, is systematic integration which represents a correlation of all significant aspects in order to achieve maximum efficiency and profit. In this respect, the question arises as to whether industrial ecosystems are a simple analogy of natural ecosystems, whether the metabolism of the systems of industrial production and consumption is an indispensable part of the biosphere, and whether the industrial ecosystems are just another form of ecosystems in which humans are the dominant species? Industrial ecology is a scientific discipline that thoroughly describes the comprehension of the environmental impact of industrial systems, as well as the interaction between the environmental and industrial systems.

Industrial ecology has diverse definitions - some authors find an analogy with natural processes or indicate the need to simulate the natural system. Industrial ecology takes into account the ecological aspect when dealing with interaction and inter-relationship both within industrial systems and between industrial and natural systems [3,4].

The paper presents a brief overview of the concept of eco-industrial symbiosis, describes the interaction of industrial symbiosis and supply chains as well as the significance of the collaboration between the participants in the supply chain in order to facilitate the implementation and development of environmentally-friendly initiatives. The paper describes one of the models of industrial collaboration in the observed region, where the result is the exchange of materials between organizational units, with the overall aim to reduce resource consumption and minimize environmental impact, and thereby reduce the amount of by-products in the industrial sector. This case study refers to the chemical sector - the production of phosphoric acid which is an important raw material for the production of mineral fertilizers, while the by-products derived from its production are further valued as raw materials for other production processes, in line with the postulates of eco-industrial symbiosis.

ECO- INDUSTRIAL SYMBIOSIS

Within the broader concept of industrial ecology, industrial symbiosis can be defined as a process that optimizes the flows of resources, energy and economic profit, through the synergy between the actors who create an eco-industrial network. One of the definitions of industrial symbiosis is as follows: "Industrial symbiosis engages traditionally separate industries in a collective approach in order to achieve competitive advantage involving physical exchanges of materials, energy, water and/or by-products. The keys to industrial symbiosis are collaboration and the synergistic possibilities offered by geographic proximity" [5].

Industrial Symbiosis is a concept that is not primarily designed for supply chains, but it can also be seen as a specific form of supply chain. In order to develop a completely closed circle where resource circulation takes place, the supply chain parties need to cooperate, which is the foundation of the concept of industrial symbiosis [6].

Industrial symbiosis supports a collective approach to the application of industrial ecology principles by enterprises in the expanded system [4,5,7]. However, the principle of industrial symbiosis encourages better linkages between organizations and helps strengthen networks in the supply chain by improving the relationships between all partners towards environmentally-friendly activities [6]. Industrial symbiosis implies the existence of at least three different entities exchanging at least two different resources [8]. Some authors have developed various models of industrial symbiosis that differ in terms of the amount of resources exchanged and the level of environmental impact [9]. According to these authors, models of industrial symbiosis can be: "a model of the planned eco-industrial park", "a model of self-organized symbiosis", "a model of reconstructed industrial park" and "a model of eco-industrial park with the concept of circular economy". The goal of each of these models is to strengthen cooperation and ecological acceptability. The principle of industrial symbiosis stimulates the supply chain participants to a high level of collaboration in order to facilitate the implementation and development of environmentally-friendly initiatives. The possibility of applying the principles of industrial symbiosis is not geographically limited to organizations of close proximity which participate in the collaboration [4]. A common geographic location is an advantage in terms of cooperation for more efficient waste management [9]; however, the most important factor for the development of the relationship between industrial symbiosis is the cooperation among the organizations because enterprises cannot implement the principles of industrial symbiosis alone [6]. The industrial symbiosis emphasizes the need for community, co-operation and connection towards an ecologically determined extended system. Social initiatives trigger symbiotic relationships and multiple mechanisms through which the partners connect and develop mutually beneficial relationships. Viewed through the perspective of supply chains, the concept of industrial symbiosis requires supply chain participants to improve their coordination mechanisms, which results in exceptional environmental benefits [10]. Industrial symbiosis effectively improves the competitiveness of an enterprise and its supply chain in terms of cost reduction and improved environmental performance, through promoting, creating and exchanging knowledge among the participants in the supply chain network, as well as through improved supply chain configurations due to the application of the industrial symbiosis principles.

In the case of industrial symbiosis, the interaction between the supply chain participants largely depends on social, information, technological, economic and political factors [11]. All relevant factors and their potential implications on the industrial symbiosis networks are presented in Table 1.

***Table 1** Factors that influence the development and operational characteristics of eco-industrial symbiosis [11]*

Types of factors	**Elements that closely determine the influence of factors on the industrial symbiosis**	**Potential operating frames of the displayed factors**
Technical-technological factors	- Physical, chemical and geographical factors in the input and output flows - Production, utilization of energy fluids, logistic capacities and the need for by-products - The availability of reliable and cost-effective technologies that enable synergy	- Number and variety of potential symbiotic connections - Achieving ecological, economic and social benefits - The volume of investments needed to develop and maintain industrial symbiosis
Political factors	- Legislation and regulations in the field of environmental protection - Taxes, fees, penalties - Subsidies and loans	- Incentives for the development and adoption of sustainable technologies and practices, as well as the incentives for developing symbiotic connections between the subcontractors
Economic and financial factors	- Prices of input raw materials, commercial value of waste and by-products - Potential revenue and economic profit - Necessary investments and costs - Maintenance of synergic systems - Current assets and return on investment	- The scope of economic advantages and competitiveness - The necessity of subsidies for renewable energy sources and recycling, and the use of waste as a potential raw material.

For the development and functioning of eco-industrial symbiosis it is necessary to establish an institutional framework, as well as to encourage the state for such alliance through national programmes of industrial symbiosis, especially in the field of using waste as a potential raw material. National industrial symbiosis programmes have been developed in many European countries: Belgium, Italy, the Netherlands, Romania, Hungary, Slovakia, Poland. These programmes involve information workshops and lectures for potential collaborators; also, potential synergies are identified and databases are created with the active promotion of synergy and analysis of results.Within national industrial symbiosis programmes, 90% synergy between the enterprises relates to the prevention and reuse of waste as by-product. In the United Kingdom, during a 10-year-long execution of the programme, the state invested 43 million EUR. Apart from a significant reduction in carbon monoxide, reduced use of primary materials and improved resource efficiency, the results of this action are economic profit, job openings and new investments [2].

CASE STUDY IN SOUTH-EAST SERBIA

Description of the technological process of phosphoric acid production from the aspect of eco-industrial symbiosis

Since its founding, the chemical industry in Prahovo has been conceived as a succession of the technological chain of copper production in Mining and Smelting Basin ”Bor”. By using sulfuric acid, which is generated as a by-product from the smelter in RTB Bor (Mining and Smelting Basin), the cycle of industrial substances has been closed and the first step towards eco-industrial networking has been made. The entire quantity of sulfuric acid produced in RTB Bor can be used owing to the production capacity of the phosphoric acid production plant. This approach has reduced sulphur dioxide emissions in the air and enabled the use of sulfuric acid as a by-product in the technological process of melting and refining copper in the production of phosphoric acid.

In the production sector of the Industry of Chemical Products (IHP) “Elixir Prahovo”, technological chain starts with the production of phosphoric acid, which is the main component for the production of mineral fertilizers, mineral nutrients, additives in the food industry, etc. The production capacity of the phosphoric acid factory is 180,000 t/year, while the current production is about 110,000 t/year with a tendency to increase.

Phosphoric acid is an inorganic (mineral) acid having the chemical formula H_3PO_4. In practice, it is commonly expressed in the form of its anhydride P_2O_5. It belongs to the medium strong acids and is obtained in the reaction of phosphate ore and sulfuric acid.

Decomposition of crude phosphates with sulfuric acid by extraction yields phosphoric acid (with 27-28% of P_2O_5) and calcium salts in dihydrate form which emerge as a by-product (insoluble calcium sulfate). The reaction in which phosphoric acid has been obtained is represented by chemical equation 1. It is an exothermic reaction which takes place in the reactor accompanied by powerful stirring and cooling.

$$3Ca(PO_4)_2xCaF_2+10H_2SO_4+2H_2O \longrightarrow 6H_3PO_4+10CaSO_4x2H_2O+2HF \quad (1)$$

By filtration, on a rotary drum vacuum filter, the phosphoric acid which contains 27-28% of P_2O_5 is transported by the pipeline system to a phosphoric acid storage site. Calcium sulfate (phosphogypsum), a by-product in the technological process of phosphoric acid production, is separated on a rotary filter, and then deposited on a pre-prepared site using a hydro-mixture (suspension). Depending on the percentage of calcium in phosphate, the amount of obtained phosphogypsum per ton of P_2O_5 is 5 to 5.5 tons. It can be further used in the construction and cement industry, but the problem related to its usage pertains to its quantities, since the amounts produced far exceed the quantities that could be simultaneously used in idustry. Compared to the current production of phosphoric acid of 110,000 t/year, the phosphoric acid production plant in IHP Elixir Prahovo produces 605,000 t of phosphogypsum. A quarter of annual production of this by-product is sold to cement factories in Serbia for the production of cement.

Due to a low percentage of active substance P_2O_5, which is only 27-28%, phosphoric acid is further evaporated to reach a concentration of about 50-54% of P_2O_5 after filtration. During the evaporation, gases that contain fluorine are released. The gas is absorbed in the devices known as absorbers, and it forms silicofluoric acid (H_2SiF_6), which is also a by-product of the reaction, i.e. the evaporation process. The absorption of fluorine is carried out by countercurrent air-water flow. The gas consists of water vapour and fluorine, whereas the presence of other chemical elements is negligible. The water in the absorber is discharged through nozzles in order to maintain greater gas / liquid contacting surface, and therefore better absorption.

Fluorosilicic acid is weak acid, corrosive to metals and very aggressive to silicon-containing substances (such as sand, concrete, glass, etc.). The amount of fluorosilicic acid obtained per ton of P_2O_5 depends on the percentage of fluorine in phosphate, its distribution and the efficiency of the absorber, but it usually ranges from 120-180 kg. The obtained H_2SiF_6 acid is in the form of a 18-24% solution and is stored in storage tanks, where it is further valorized for the production of aluminum-fluoride, which is a new product. Aluminum-fluoride (AlF_3) is an inorganic compound used in the production of aluminum, and also as a means of reducing the electricity consumption. In its further development projects, IHP Elixir Prahovo has planned to perform the reconstruction of the AlF_3 plant, in order to utilize fluorosilicic acid which is produced as a by-product in the process of concentrating phosphoric acid.

The given example has displayed the following advantages:

- Emissions of polluting substances have been reduced – therefore, water pollution and emissions of harmful gases have also been reduced;
- The use of secondary materials has been increased – therefore, storage costs have been cut down, and by-products have been used as material inputs which reduced the need for natural resources.

CONCLUSION

Due to the existing infrastructure, current business models and technology, as well as due to the grounded behavior, the economy becomes "trapped" in the linear business model. Industrial symbiosis accelerates the development of the economy moving it from a linear to a circular model; however, business entities lack the information and the capacities to accept the solutions provided by circular economy [12]. Instead of relying on solutions focused on the use value of products, circular economy eliminates waste at the design stage and fosters innovations throughout the life cycle of the product.

The paper explains the mechanisms for establishing a collaboration between industries, and provides an overview of the diverse factors that could influence the synergy between the industries to a small or a great extent. In the example of phosphoric acid production, the partners have created mutual agreements for several reasons: due to lower prices of potential raw materials, minimization of storage costs of by-products and greater environmental responsibility. Development of the described business model significantly contributes to the zero waste concept, while the practical example of the collaboration of participants within the chain of eco-industrial symbiosis can promote the emergence of industrial clusters whose target would be the exchange and use by-products as a valuable raw material for another production process.

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VISUAL POLLUTION OF URBAN AREAS AS ONE OF THE MAIN ISSUES OF THE 21ST CENTURY

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Abstract

When there are words about pollution and culmination point it has reached in 21st century that we live in, it is mostly about physical pollution, i.e., pollution of air, water and soil. However, visual and noise pollution are increasingly mentioned, and although younger than previous ones, today reach unimaginable proportions in urban areas. This paper is going to analyse visual pollution, widely present in urban areas. Visual pollution is current, in smaller or larger amount, in almost every space that people spend their time in. However, cities are areas where this problem culminated and has great negative influence on quality of life. This paper's goal is to raise awareness about potential problems that visual pollution creates, identification of negative influences and consequences it has on life comfort, but also analysis of potential solutions, which would reduce or completely remove these problems.

Keywords: Urban pollution, Visual pollution, Quality of life, City

INTRODUCTION

Pollution is old as the man's will to create settlement and rearrange space according to his wishes and needs. James Septh defines it as harmful – too much of something in the wrong place, and categorizes in four 'traditional' ways – by receiving media, sources, types of pollutants and effects that pollution has on its environment 0.

Physical pollutants have instant effect, which often makes them induly inferior over noise and visual pollutants. Psychological effect is equally harmful, but often neglected, because its influence is revealed in time and almost impossible to remove.

The values of one phenomenon can be classified by economic, legal, political, ethical, historical, aesthetic, religious, etc. 0. Visual pollutants are defined as any physical barrier that interrupts clear sight line, or distracts attention from unique space qualities. Despite the fact that during the analyses of visual pollutants mostly economical, aesthetic and ethical values are considered, we cannot neglect historical values, since historical monuments are regular victims of visual pollution. Visual pollution could, in that sense, be defined as damage to the environment in a way perceivable to the human eye, coupled with psychological effect on human being as user of space. Receiving media in this case is every message that user has received. Researches show that people note up to 400 advertising messages in one day 0.

This paper identifies and analyses negative influences visual pollution has on users of certain polluted space.

THE EFFECTS OF VISUAL POLLUTION

Effects that visual pollution has on life quality of people could be discussed form few aspects. Not only that visual pollution has influence on users of the space as individuals, it also damages the atmosphere of a certain space as a whole and has great influence on loss of its identity. Towards better understanding of these effects, analysis was conducted. Likewise, similar world cases were exposed, which, in smaller or greater amount are successfully dealing with this problem. In order of better understanding the influence visual pollution has on the environment, a survey based on responses of citizens of City of Niš was conducted.

The negative influence of visual pollution can be diverse, and usually represents distraction, identity loss, eye fatigue, reduction of natural diversity and comfort of space, influence on attractiveness of a certain space, etc. Excessive consumption of advertised products, shopping adiction, consumption of unhealthy and fast food which leads towards obesity and a series of deseases.

This paper is exclusively on influences that visual pollution has on a space as environment that one individual uses. In that sense, effects are classified into three groups by their influence on a space as architectural entirety, its ambient, or identity of a space.

Disruption of the identity of a space

Identity of a city is created by people – users of that space, during certain period of time. City design is type of permanent art. In every moment, there is more than eyes can see or ears can hear, so we explore every space. However, none of certain space's elements could be perceived on its own, but as a part of a whole, environment in which we occur 0.

According to some theorists of modern psychology, identity is special state, characteristic for individual subject or society. It develops from the relationship between that individual (or society) and some external influences. However, this uniqueness or any other identity characteristics hardly could be perceived in highly visually polluted areas 0.

Influence that visual pollution has on identity of a certain space could be displayed on the example of South American city São Paulo (Figure 1). This city implemented special law in 2007. – 'Clean City Law', which prohibits all alterations, billboards and advertisements, in order to clean the city and its facades. 'Clean City Law' has, shortly after its implementation, become very popular among citizens. As much as 70% of them approved its implementation, and huge number of people admitted to see the city in entirely new light, or not recognizing some streets after their cleaning 0.

a) *b)*

Figure 1 *Photographs of São Paulo before and after law implementation a) before; b) after 0*

Disruption of the atmosphere of a space

Peter Zumthor describes atmosphere as our first reaction, impression that happens in a fraction of a second 0. However, the atmosphere, although perceivable in a single moment, is built over time, and often demands long sequence of decades, even centuries, so it could reach its today's shape. The quality of urban environment, among other, includes its visual quality. This feature directly stems from aesthetics and comfort a certain space can offer on its user 0.

The City of Niš, is third largest city in Serbia, and one among examples of cities fighting with high level or visual pollution. The main city street is just one in sequences of city features that have lost their role of representative areas. This city's communications are, due to opening of gardens of cafes, reduced to edges, and facades are almost imperceptible, because of inscriptions and advertisements, but also large canopies, which represent significant visual barrier.

We must also mention the city of Barcelona, as one of the most attractive touristic destinations in Europe. This city has, due to uncontrollable street art and damaged facades, and in order to cherish its cultural goods and characteristic atmosphere, conducted the project under the name 'Barcelona posa't guapa'. During this project, a large number of objects, among which were Casa Milá and El Arco del Triumfo, were cleaned and restored 0.

Disruption of life qualities of space users

The negative influence that visual pollution has on the life quality is multiple. It could be distraction, eye fatigue, physical or visual interference, intolerance towards certain space, and similar 0. According to Jana *et al.* 0, children that grew up in highly visually polluted environments, have damaged aesthetic senses and have no need to stay in pleasant space. Also, one more negative effect of this pollution is perceived in its influence on peoples' ability to understand the quality of their environment, and capacity to reduce their need to improve it.

We cannot, as well, ignore the danger of billboards located near busy roads. Especially digital billboards attract drivers' attention away from the road and place them and passengers in great risk. On the other hand, installation cables, often stretched above peoples' heads, beside visual barrier, represent physical danger, and often are obstacle to emergency vehicles which, because of them, cannot reach objects.

RESEARCH OF THE VISUAL POLLUTION OF THE CITY OF NIŠ

Visual pollution of the City of Niš is evident and highly expressed. Beside shiny advertisements located on objects' facades, billboards are also dominant. Gardens of cafes halved the street and brought communications to edges so objects can't be fully perceived 0.

In order to better understand the effect visual pollution has on the quality of residence in a certain space, and with special accent on perceptibility and clarity of architecture opposite to advertisements and alterations which, often, overlap it and make it unavailable to the eyes of people, the survey was conducted upon residents of Niš. In this survey participated members of both genders, of most diverse professions and all age groups. 50 people participated. The youngest participant was 18, and the oldest 67 years old. Photographs of three objects in Niš, which were previously in software Adobe Photoshop, cleaned of all advertisements and alterations, and their surroundings removed, were shown to respondents. Objects included in this survey were: 1) Object in Obrenovićeva street under the number of 38., built in 1927. by the project of Julian Djupon (Figure 2); 2) Object in Obrenovićeva street under the number of 37., built in 1921., which today holds The International Red Cross and Red Crescent

Movement Offices (Figure 3); 3) Object under the number of 17. Known as The House of Andon Andonović, built in 1930. by the project of Belgrade architect Milutin Borisavljević (Figure 4). All three objects represent extraordinary examples of architecture made in the period between two World Wars. Respondents were asked to write, under each object, in which city in Europe they think object is located. Survey results are displayed in Table 1.

Figure 2 *Photograph of the object 1) left: object in its current state, right: display of the same object but without advertisements and environment, Photo and treatment: M. Cvetković*

Figure 3 *Photograph of the object 2) left: object in its current state, right: display of the same object but without advertisements and environment, Photo and treatment: M. Cvetković*

Figure 4 *Photograph of the object 3) left: object in its current state, right: display of the same object but without advertisements and environment, Photo and treatment: M. Cvetković*

Table 1 *Survey results*

	Niš	Other city in Serbia	City outside Serbia
Object 1)	10	14	26
Object 2)	24	11	15
Object 3)	11	/	39
	45	25	80
			45/150

After the survey, interview was conducted with every of respondents, in order to understand their opinion about visual pollution in city they live in. From them was expected to state their beliefs about cleaning the city from all alterations and advertisements, and restoration of the facades. Their answers were categorized in three groups: a) those that approve cleaning the city from ads, b) those who believe that there is no need for such intervention, c) those that do not have any opinion. Interview results were displayed in a Figure 1.

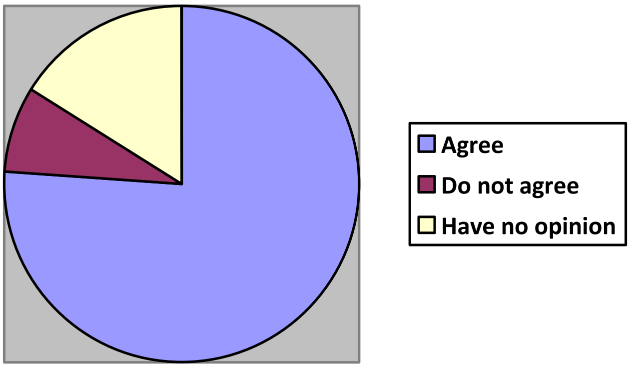

Figure 1 *Interview results*

DISCUSSION OF THE RESULTS

Results of conducted research show that, due to incomprehensibility and overflow of the space which they occupy, people are not capable to identify it. Obrenovićeva street, in which analysed object are located, represents the centre of the City of Niš and the most crowded communication which, at first sight, has to offer a lot of activities and benefits. However, it could be noted that the quality of these contents is endangered due to negligence of the space and misunderstanding of its qualities. Beside coffee shops, there are almost no longer holds in this space. This city mark in larger amount serves as a place for shopping, so its users do not have opportunity to feel the atmosphere and enjoy unique ambient.

However, encouraging fact is that large numbers of people recognize the problem and have a desire to improve and promote their environment. Up to 76% of respondents agreed that the City of Niš can offer much more than what it offers now, and all of them displayed the desire to, in some way, participate in improvement of the space they are using almost daily. 8% of the respondents don't have any problem with the current state of the city, which they explain as 'development of certain city in accordance with modern era'. 16% of respondents declared their opinion as neutral.

CONCLUSION

Visual pollution is increasingly present in urban areas. It is usually the result of negligence and disrespect of cultural heritage, but also uncontrollable economy development and intention of companies to attract more customers. Advertisements are becoming more and more conspicuous and visually aggressive, with the attempt to attract potential purchasers. Increasing billboard sizes, light and sometimes sound effects, inappropriate locations for their displacement on historical monuments are leading to bigger visual pollution of city centers. It is necessary to understand negative influences that economy has on environment and quality of life of people as users of a space. In that sense, it is important to educate people about its disturbances, but also stimulate their sense for aesthetics. Quality and diverse space, does not only influence the mood of its users, but also, with its uniqueness, contributes to attractiveness of a city as a whole, and thus, development of economy and tourism.

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USE OF NON – EXPLOSIVE MATERIAL FOR CRUSHING AND CUTTING

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Abstract

This paper describes the material - expansive mortar (FRACT.AG.C) in cartridges pack for demolish and cutting rocks and all type of concretes. Also are given some results of use in the queries in Macedonia for white marble and impact to environmental with accent of environmental protection and policy.

Keywords: Mortar, Non explosion, Cutting, Demolish, Marble

INTRODUCTION

FRACT.AG is a highly expansive mortar to demolish and cut rocks and concretes. FRACT.AG swells when poured into a hole and develops a pressure higher than 8000 t/m^2 on the hole walls, thereby breaking them open. FRACT.AG is **environmentally friendly** because it releases no toxic fumes or harmful substances of any kind. It is non-explosive, therefore supervision of trained personnel is not essential. FRACT.AG storage requires no special precautions, provided the containers are not tampered with and are kept in a dry place.

The product is not sensitive to electrical discharges or currents.

On the market are any types of this material or agent. There are six types of fract.ag like powder and plus type with cartridge for horizontal holes.

In this paper we give some characteristics and way of use for the expansive mortar pack in cartridges.

Some characteristics of material

This material, FRACT.AG can be used in an unlimited range of applications and particularly to break, cut, or demolish rocks, concrete and reinforced concrete when explosives cannot be used for safety reasons. This is clean $CaCO_3$ dehydrated and baked in high temperature over 1600ºC and milled in fine granulation in the form of powder.

We can used on any type of rocks formation, concrete or tiled structure in: excavating foundations, leveling rocks for road works removing boulders, different demolitions for buildings, poles, towers, walls etc. Also this is very important: can be used for cutting blocks of marble, granite and travertine more economically than with the traditional helicoidally wire cutting method and excavation and demolition of rocks formation or cement/concrete structures where the use of explosives would be expensive due to long operating times, special transport, more secure and safety ways, storage and handling precautions and the need to comply with public safety regulations. This material are produce with different commercial names. Most popular is this tip FRACT.AG, from the firm CHIMICA EDILE, srl, Italy.

Six types of Fract.AG are available on the market. This all types are in use depends of temperature in the air when we use.

Figure 1 *Pack of cartridges types of frack.Ag C*

On the market are any types of this material or agent. There are six types of fract.ag like powder and plus type with cartridge for horizontal holes.

Depends of temperature in the air, this types can be used.

For format with cartridges are this types:

RED – for near 5°C, GREEN – for temperatures from 5 to 25°C, YELLOW – from 20 to 35°C, GOLD – for 35 to 50°C, BLUE – 50 to 60°C or universal and SILVER types for high temperatures.

The product in cartridges is conveniently supplied ready – mixed in plastic wrapped cartridges and as such there are no limitation to its use in any working environment. Mixing is not necessary thereby eliminating the possibility of using the wrong amount of water, since it will only absorb the required amount. It can be used anywhere without taking special measures (roofs or wall holes). Reaction time is quicker, therefore it demolishes or cuts faster. Cartridges are available in 100 cartridge – boxes. Each cartridge is f 28mm, 22cm long and contains 200g of agent. They **must be used** in 32-34mm diameter holes. 100 cartridges are enough for a length of 14 to 16 meters of holes.

Goggles and rubber gloves should be worm as a safety precaution. This is an alkaline product with a pH = 13 and could cause severe irritation to mucous membranes, especially eyes.

Tips on how to use the cartridges

When we use FRACT.AG must to know tips for best useful. The distance between the centers of the holes in the rock (marble or granite) or non-reinforced concrete should be 30 to 60cm, depending on the diameter of the holes. (for example: f32mm dist.= 30cm, 35=40cm, 40mm=50cm). For the best possible use and to obtain best results it is advisable to carry out preliminary tests with FRACT.AG before starting work.

Estimated consumption of FRACT.AG powder in cartridges for 1meter of hole is:

Diameter	30	32	34	38	40	45	50
Consumption (kg/m’)	0.9-1.0	1.0-1.2	1.5	1.8	2.0	2.6	3.0

When we use this agent must keep our face from the hole during the first 2-4 hours as the product might (thigh highly unlikely) eject from the hole violently (blow-out) if instruction have not been followed correctly.

When used in highly absorbent materials like **concrete,** the holes should be dampened before the mortar is poured, making sure however, that there is no presence of water.

Mixing is not necessary thereby eliminating the possibility of using the wrong amount of water, since it will only absorb the required amount. It can be used anywhere without taking special measures (e.g. roofs or wall holes. Reaction time is quicker therefore it demolishes or cuts faster.

Who can use and where FRACK.AG C?

This is material – highly expansive mortar to demolish and cut rocks and concretes. When is purred into a hole after some time (3 to 8 hours depends of temperature) develops a pressure higher then 8000t/m^2 on the hole walls.

It is non explosive material, and for storage requires no special conditions, provided the containers are not tampered with and are kept in a dry place.

FRACT.AG C can be used in an unlimited range of applications and particularly to break, cut, or demolish rocks, concrete and reinforced concrete when explosives cannot be used for safety reasons.

We can used on any type of rocks formation, concrete or tiled structure in: excavating foundations, leveling rocks for road works removing boulders, different demolitions for buildings, poles, towers, walls etc. Also this is very important: can be use for cutting blocks of marble, granite and travertine more economically and easily way than with the traditional helicoidal wire-cutting method and excavation and demolition of rocks formation or cement/concrete structures where the use of explosives would be expensive due to long operating times, special transport, more secure and safety ways, storage and handling precautions and the need to comply with public safety regulations.

In general, anyone can use it in any situations, because it is perfectly safe, soundless and nonhazardous. It does not debris or dust, not does it form gas or cause any shock waves. Unskilled labor can be very easily trained to use in a short time. FRACKT.AG in powder form in the bags of 5kg and 20 kg is a powder that must be thoroughly use with clean cool water. Powder (5kg bags) of this material mixed in a ratio of 30% of the overall weight. Put the required amount of water into a large container (1.5 liters for each 5 kg package), gradually add the powder to water stirring all the time to obtain a smooth, lump free mortar. Pour the mortar into the prepared holes within 5 to 10 minutes.

Way of use

The necessary number of cartridges (depends of total length of holes) dip in a bucket of clean water at the correct temperature (check type of fract.ag.C selected) for approx. 3 – 5 minutes. Insert the wet cartridges in the holes one at the time, one by one, packing them in tightly with a rod to make them adhere to the wall of the hole.

a) b)

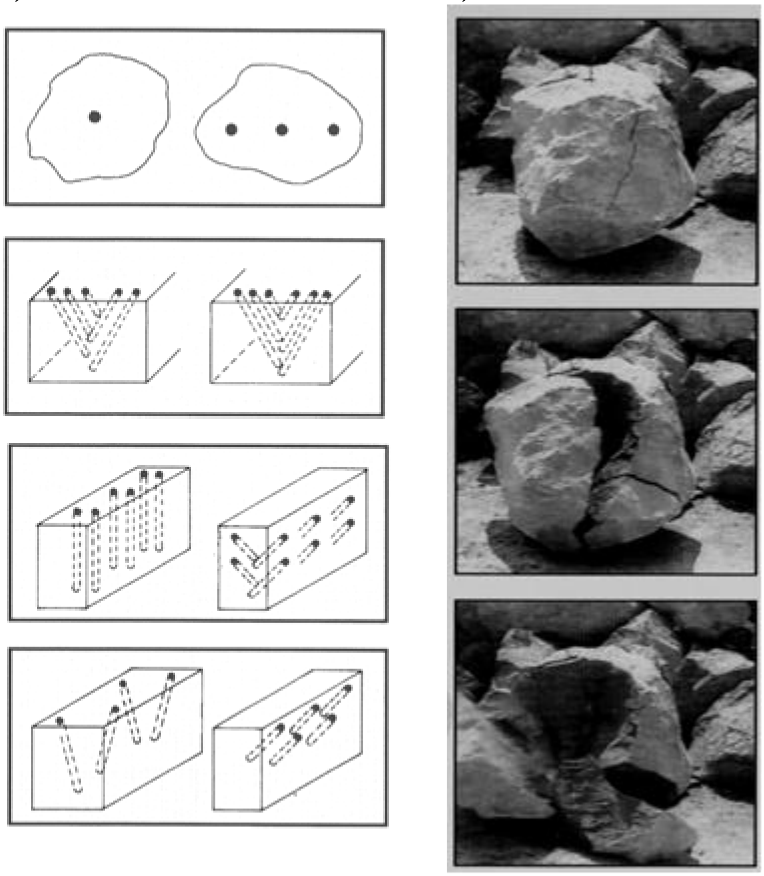


Figure 2 *Ways of use fract.ag C (for demolition, cuts, splitting, breaking rocks)*
a) ways of use in the blocks for demolition and b) breaking big blocks

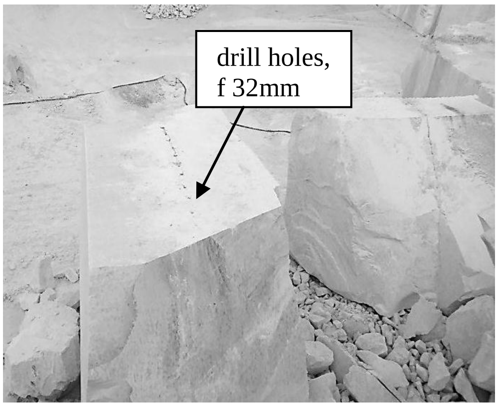
In the last cartridge once inserted, should not fit, remove it, and using your hands, fold it in half and break it in two pieces which can then be used to complete the filling of two holes.

a) b) c)

Figure 3 *Block – lamellae of white marble ready for cutting with 5 row of holes, b) cartriges in water, c) put in the holes*

Results from tests with frack.ag C in some quarries for marble and granite

This material is in use in some queries in Macedonia. They use this type for cutting big blocks to commercial dimension. After cut the place of cartridges (empty holes) is only with white color and hard calcium carbonate.



Block with holes before use cartridges | Crack between new blocks | New fresh site of the block

NEW FACE IN THE COMERCIAL BLOCK AFTER ACTIVITY OF FRACT.AG.C

Figure 4 *Results from action with FRACT.AG.C in some queries in MK*

CONCLUSION

This material (base is $CaCO_3$) can use in any situation for more methods for cutting and splitting blocks in the quarry mine. Also this agent we can use for demolition concrete/cement structures. This method is more economically than standard methods of cutting blocks of marble or granite. The time for action effects depend of weather and temperature on the blocks. This time was between 3 and 12 hours for our tests which we make in this quarries.

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ECONOMIC INPUTS AND OUTPUTS OF URBAN GARDENS: LITERATURE REVIEW

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Abstract

Growing fruits and vegetables in community and home gardens has often been advertized as an economically viable activity that allows urban households to make or save money. Still, there are not many reliable sources to document the actual inputs and outputs of such gardens and track the amount of food produced and production costs. The paper reviews the existing literature on economic viability of community and home vegetable gardens, specifically looking into data collection methods and factors influencing the net value of gardens. The study has demonstrated a limited number of academic papers in the field of research, with only 7 articles published in English between 1985 and 2018 accessible via selected electronic database. Investigation of the methods applied in each study indicates the importance of participative tools in data collection and analysis, as they represent a reliable and democratic approach to research. Results of the studies suggest there is a considerable potential of urban gardens to provide important amount of food for gardeners and their families. Results cannot be generalized because they depend on various factors such as weather, crop selection, cultivation techniques and gardeners' skills. The future research could look into correlations between those variables in order to enable extrapolation of results up to different scales.

Keywords: Community gardens, Home vegetable gardens, Economic viability, Methods, Review

INTRODUCTION

Vegetable gardens are often promoted as a way for households to save money [1]. Still, little is known about the actual inputs and outputs of urban gardens. In recent years, there is a growing interest among researchers to quantify the amount of food produce and gardening inputs in terms of land, labour and capital [2-4].

Nugent [5] outlines economic model to examine the reasons why households engage in urban gardening and to explain the factors that influence economic viability of gardening. Households jointly decide how to allocate their resources - time, money, labour. However, the economic model becomes much more complex when facing reality. Urban gardeners are, unlike in other economic activities, simultaneously suppliers of labour, producers and consumers of food. It is also important to keep in mind that benefits of gardening extend beyond economic benefits [1].

Even though surveys indicate that saving money is one of the most common reasons why people engage in urban gardening [6] and the economic outcomes of gardening are assumed favourable [7], there is little evidence that value of yields compensates for the inputs. Only a limited body of research empirically investigates crop yields and financial investments in gardens [2,8]. Documenting yields of urban gardens is important to help determine their role in local food economy [8] and food security of urban population. It is important to monetise the yields, as most of the production and consumption of food coming from urban gardens belongs to informal economy and is not otherwise tracked [8].

The reliability of research methods used in documenting economic variables, such as yields and inputs, has not been coped with in detail in the literature [9]. Economists and even gardeners themselves find it hard to explain and evaluate the economic benefits gained through gardening [10,11]. The study of home gardens in the city of Kragujevac illustrates the ambiguity and confusion gardeners experience when asked to evaluate economic benefits of their gardens - those who had initially identified the economic motives as main reasons for growing their own fruits and vegetables, later expressed doubts whether their gardens are at all economically viable [11].

Given the re-emerging importance of urban food production and the growing academic interest for the topic, this paper attempts to methodically review the existing literature on economic inputs and outputs of urban gardening, focusing on methods and reliability of data. The author has identified one review paper by Langellotto from 2014 [1] that coped with economic costs and yields of home vegetable gardens. Four out of six resources were more than 25 years old, dating back to years before 1985. Conversely, this paper investigates research articles published in years after 1985 and includes both community gardens and home vegetable gardens. The aim of the review is to extend the knowledge by specifically looking into: 1) methods applied, 2) output value of the gardens, 3) costs of gardening and 4) net value of garden plots. The purpose of the paper is to identify gaps in existing bibliography and to imply future research directions in reference to variables assessed in the review.

MATERIALS AND METHODS

The research applies systematic quantitative methodology of literature review [12]. By using systematic approach, the review provides replicable, reliable assessment of the current state of the field of research [12]. The literature is searched and categorized methodically. The results document geographical scope of research articles, methods applied and the types of results obtained [12].

The paper presents a review of the academic articles on economic viability and food production of urban gardens, published in English between 1985 and 2018. The articles have been identified and selected via searches of electronic database of Google Scholar, Science Direct, SpringerLink, Journal of Extension and HortScience. The search was performed between December 2017 and April 2018. Combination of keywords such as 'vegetable gardens', 'gardening outputs', 'economic', 'value', 'costs', 'food production', 'quantify' was used for searches. Only studies that quantified food production of urban gardens and detailed methods of data collection and analysis have been considered. Moreover, the search included relevant literature that appeared in references of the selected articles. The review considered both community gardens and home vegetable gardens. The papers results were triangulated against relevant literature sources on economic viability and food production of urban gardens.

A total of 7 research articles were reviewed (Table 1). Data were collected and systematically organized in tables. The author performed descriptive statistics to analyze methods applied and data on economic inputs and outputs of the gardens. For each article, the author identified and documented the following data: names of the authors and the year of publication, location of the garden, type of garden, method applied in the study, value of the produce, costs and net value of the garden plot (Table 1).

RESULTS AND DISCUSSION

All the reviewed articles studied gardens in North America, in the USA and Canada (Table 1). One of the papers drew comparison between gardens in Paris and Montreal [3]. Cleveland *et al.* [13] looked specifically into food production in an arid region, with low annual rainfall and very high potential evapotranspiration throughout the year.

Two articles investigated home vegetable gardens, while other five coped with community and allotment gardens (Table 1).

A common subject of some of the reviewed articles is the correlation between food produced in the gardens and gardeners' dietary habits [3,7]. Gittleman *et al.* [8] focused on the methods and challenges involved in conducting participatory research. Blair *et al.* [7] studied correlation between gardening and dietary habits of gardeners, life satisfaction and neighbourhood involvement. Cleveland *et al.* [13] performed an experimental plot study of two home vegetable gardens to measure gardening inputs and outputs and determine whether gardening can provide savings. Algert *et al.* [9] studied vegetable outputs and cost savings of community gardens in order to understand the capacity of community gardens to provide food for urban population and affect local food economy. Similarly, CoDyre *et al.* [2] attempted to extrapolate results up to the city level in order to estimate the role of gardens in food security of urban population.

One of the major methodological challenges concerning research of economic viability of urban gardening is collection of reliable data on quantities of food produce. There are two distinct research approaches to data collection. The authors either measured or recorded the weight of garden produce, having gardeners actively involved in data collection, or estimated values based on the norms of conventional agriculture yields.

Two of the research articles performed participatory research method of citizen science [8,9]. Both studies applied the toolkit provided by Farming Concrete project[1]. Citizen science is a democratic approach to studying food production in community gardens, giving a community a certain power to decide what is being studied, how it is studied, to participate in collection of data and the conclusions drawn from the research [8]. Participants collected data in one or both ways: weighing produce throughout the season (Harvest Kit) and counting plants at one to three points in the growing season (Crop Count Kit) [8]. Counting plants included recording number of plants per crop and dimensions of areas under each crop. Data on harvest weight and numbers of plants allowed for calculation of an average yield per plant and average yield per square foot, which helped estimate production of other gardens as well. Researchers then monetized the yields using average retail prices of vegetables. Costs were documented from memory and included investment in plants, seeds, fertilizers, tools and soil amendment [9]. The method is replicable.

CoDyre *et al.* [2] performed a variation of participatory method. Gardeners were asked to keep a “garden diary” in order to document how much food they produced and inputs (such as time, space and money) invested in the garden [2]. Gardeners recorded estimates of the volume of vegetable produce and counted and recorded their number. Each estimate of the volume was later converted into weights of each vegetable based on the average weights of similar produce in local grocery stores.

Two of the reviewed articles performed estimation of yields without measuring the harvest. Blair *et al.* [7] assigned a potential yield on a scale of very good (90% of potential yield) to

[1]Farming Concrete is an open, community-based project aimed at determining the amount of food produced in the community gardens in New York, by involving gardeners in the process.

poor (25% of potential yield) to each planting they monitored. The economic value of vegetable produce was calculated using formula:

expected yield/plant x assessed number of plants grown x assessed potential yield (0.90 to 0.25) x 1987-1988 dollar market value.

Patel [4] used USDA formula to estimate monetary value of food produced in gardens:

monetary value of production = garden area x crop intensity (distance between rows) x crop quality x length of season (frost - free days).

Estimation of potential yields is a less reliable method because of the many variables that need to be considered such as environmental conditions (soil, water, and sunlight), growing techniques, types of crops [8]. Harvest booklet is a reliable tool for evaluation of the levels of food production in gardens, though it is highly demanding tool that requires commitment of the gardeners throughout the season on weighing the produce and writing it down [3]. In either case, the results of the research cannot be generalized and applied to other cities [2] because of the many factors that influence the productivity of gardens.

Pourias *et al.* [3] used combination of two approaches in data collection. The authors had gardeners record units of harvest to be converted into grams and a sample of gardeners record both the number of units and the weight in grams, latter to be used as a reference value for estimation of the yields in the rest of the sample.

Cleveland *et al.* [13] conveyed an experimental plot study. As such, their research method is not replicable.

Gardening costs included investment in plantings, seeds, tools, fertilizers and soil amendments [9]. CoDyre *et al.* [2] determined that the investments in gardens vary greatly with an average cost of $10.82/m² including expenditures on soil, fertilizer, plants and seeds. The study, however, included gardening in pots which is costly. Conversely, Langellotto [1] in her review paper on economic costs and benefits of home vegetable gardens indicated that costs of materials and supplies were relatively steady across gardens, in comparison to yields. Some authors documented the time spent in the garden in order to estimate costs of labour [2, 13]. In her review, Langellotto [1] suggested that vegetable gardens are profitable if the labour value is excluded from the costs of gardening. Cleveland *at al.* [13] have reached similar conclusion, suggesting also that 2.1 to 2.9 hours of work per week in the garden would be sufficient for gardeners to save money.

There are considerable variations in yields from one garden plot to another [2,3,7] (Table 1). Number of factors influences the productivity of gardens and causes the inconsistent research results, such as types of crops, weather, soil conditions, gardeners' skills, availability of water, gardening practices [3,4,8,9]. Though some authors have brought into correlation garden yields and savings with the size of the plot [4], Pourias *et al.* [3] suggested that the size of the plot is not a reliable indicator of the productivity of a garden. It is rather gardeners' motivations that influence the size of the garden dedicated to food production [3]. CoDyre *et al.* [2] suggested that the low efficiency of gardens and ultimately low yields came as a result of poor gardeners' skills. The more experienced gardeners, with more than 7 years of experience, were more productive than the less experienced ones. Selection of crops affects the overall productivity of gardens. Tomato is one of the most profitable garden crops [1]. Other profitable crops are leafy green vegetables, peas, strawberries, squash and eggplant. The most common crops grown in reviewed gardens are tomatoes [2,3,8,9], squash [2,8,9], beans and green beans [3,9], peppers, onions, eggplants and cucumbers [9]. Economic viability of gardens depends greatly on the weather and climate condition. In the arid region of Arizona water was the largest expense, making almost 30% of the total costs of the gardens [13]. The length of the growing season is an important factor as well [3,4].

***Table 1** Collected data on reviewed papers*

Authors	Location	Type of gardens	Vegetable output	Labour costs recorded	Other costs per year	Produce value per year	Net value per garden per year
Algert *et al.*, [9]	USA, San Jose	Community gardens	*3.66 kg/m²	-	-	$435 per plot	1.
Blair *et al.*, [7]	USA, Philadelphia	Community gardens	-	-	$47 per person	$160 per garden	$113
Cleveland *et al.*, [13]	USA, Tucson in Arizona	Home vegetable gardens	1.24 kg/m², 2.31 kg/m²	yes	-	-	$109, $123
CoDyre *et al.*, [2]	Canada, Guelph	Backyard gardens	1.43 kg/m²	yes	$10.82/ m²	$4.58 / kg	-
Gittleman *et al.*, [8]	USA, New York	Community gardens	*5.86kg/m², *1.61 kg/m²	-	-	*$32.26/m², *$12.37/m²	-
Patel [4]	USA, Newark, New Jersey	Community gardens		-	$25 / garden	$504 per garden	$475
Pourias *et al.*, [3]	France, Paris and Canada, Montreal	Family g., shared g., commun. gardens	1.2±1 kg/m², 1.4±1 kg/m², 1.9±1 kg/m²	-	-	-	-

*The author converted values using 1 lb/ft² = 4.88 kg/m² and 1 ft² = 0.093 m².

Net values of garden plots vary considerably. Some of the authors reported positive net values ranging from $113 to $475 per garden per year [4,7] (Table 1). CoDyre *et al.* [2], however, suggested that the production of vegetables in studied gardens costs more than the same produce in the local grocery store. The average gardener was paying a 39% premium to grow his or her fruits and vegetables. The authors did identify considerable potential to produce high yields if the gardening skills would improve. Conversely, Pourias *et al.* [3] confirmed relatively high yields in community gardens they had studied. The study of Gittleman *et al.* [8] indicated that gardening practices in community gardens in New York are closer to „biointensive" farming than to large scale industrial farming [8]. Findings of Algert *et al.* [9] suggested that the community gardening practices in gardens of San Jose are similar to high-production agriculture.

CONCLUSION

Results of the studies illustrate the potential for and current capacity of urban gardens to provide important amount of food for gardeners and their families [8]. Almost all of the studies documented relatively high yields. There are, however, considerable variations in yields from one garden to another. Costs are quite steady in comparison to yields. One of the common conclusions is that gardening can save money when opportunity labour costs are excluded from calculations.

Some of the studies conducted participative methods to include gardeners in various stages of the research process. The citizen science approach does not only offer reliable data and is a replicable method, but it encourages scientists to work directly with people who have a stake in research outcomes. Involving relevant stakeholders can improve quality of gardeners' participation and contribute to development and spread of similar research projects [8].

Results of research cannot be generalized because they are affected by various variables such as weather, crop selection, cultivation techniques and gardeners' skills. This means that the results are relevant only to the years the data are registered and only to those gardens that are inventoried. In order to be able to extrapolate findings to gardens citywide, more data is needed. The future research could also look into cost savings and yields for specific crops [9].

Quantifying food production in urban gardens is valuable to various stakeholders [8]. Community gardens can use the information of their monetary value to increase their visibility, to apply for funding and build capacity to even increase the amount of food produced in the gardens. In broad terms, data on food production quantities and economic value of community gardens can serve as an incentive for the development of new and preservation of the existing gardens. Such studies can also inform policies related to urban agriculture [8].

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LAWN STRUCTURE IN THE AREA OF ”BISER” NAUTICAL VILLAGE, BOLJEVCI, BELGRADE

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Abstract

In recent years, more attention has been paid to the green areas of tourist resorts, areas that are rich in preserved natural and cultural resources crucial for the development of tourism. The existence of "Biser" nautical village should contribute to higher visitor numbers, tourism and economic development of a wider environment. Lawns make up the largest percentage of the area of a nautical village and are very important for the entire area. Lawn structure analysis defining the existing state of grass surfaces as the first step towards improving their quality. The method of work included collecting literary data, field research, synthesis of collected data and conclusions. The survey was carried out during year 2017. A total of 42 plant species were observed. The largest number of recorded plants belongs to a group of other herbaceous plants (59%), a much smaller number belongs to the category of high-quality grasses (10%). The high presence of species belonging to a group of other herbaceous plants and bad quality grasses points out on the low level of lawn care and maintenance of recreational areas. Based on the analysis of the lawn structure, guidelines are given for improving and conserving the greenery of the nautical village "Pearl". The conclusions will serve as a theoretical framework for further development and improvement of the lawns of a nautical village, as well as the development of tourism in this area.

Keywords: Green area functionality, Lawn, Urban greenery, Lawn maintenance

INTRODUCTION

Nautical tourism belongs to a specific form of touristic movements and resolves a specific type of touristic needs, which manifests itself through the need for leisure, recreation and satisfaction the cultural aspect of the tourist need [1]. Under the object of nautical tourism, there are acceptance object facilities and craft shall [2]. There are different categories of acceptance object facilities in nautical tourism among which the most famous and most represented are tourist marinas [3]. Tourist marinas have become popular because apart from devices and equipment, provides a range of different, supplementary services. Marinas, according to the green area classification of each city, belong to the public use objects of landscape architecture [3]. These types of open public spaces represent the natural and cultural resources of the society in the city environment [3]. As a specific type of green urban area or in the city vicinity, they marinas a major impact on the modification of microclimate conditions and the sanitary comfort of the inhabitants [4].

The specificity of the greenery in "Biser" nautical village is besides aesthetic, recreational, health and general enhancement functions, additional a social, sanitary, hygienic and engineering-technical function. Nautical village "Biser" is used for active and passive recreation and improves the quality of the user's environment. Lawns represent the largest percentage share of greenery in each urban area [5] like in the area of nautical village. A review the lawn structure and the relationship between plants within and gathering data of the distribution of plant species, specifics of lawn types, the nature of lawn care and maintenance, in order to provide a useful baseline for achieving better lawn functionality and urban greenery in general [6].

Sports and recreational green areas are parts of preserved and “healthy“ landscapes [7] and with absence or low care and maintenance measures the value of these areas, as well as the quality of the urban environment decrease. A detailed analysis of the lawns of the "Biser" nautical village in Boljevci is of great importance for the improvement of the existing green areas. The aim is to review a current situation and the lawn structure on green areas of research site, define the proper lawn care and maintenance measures, to improve the entire space of "Biser" nautical village. This type of green area represents a specific form of public spaces that is of great importance for creating a quality and interesting space [3].

MATERIALS AND METHODS

In "Biser" nautical village floristic composition and lawn structure were performed according to 8 phytocenological records (Table 1). The number and location of the records was determined by the diversity of the floristic composition and the uniform coverage of all parts of the investigated area: 1. in front of the restaurant entrance; 2. on a slope along the Sava River (coastline); 3. within the football field; 4. within the volleyball court; 5. in front of the reception desk; 6. along the sidewalks; 7. lawn of traffic roundabouts; 8. near the forest edge.

The floristic research was performed during 2017 using the standard phytocenological method of the central European school of Brown Blanquet [8]. Plant identification was carried out according to the following reference sources: Josifović et al. [9], Šarić [10], Kojić [11], Mišić *et al.* [12], Stavretović [5]. Recorded plant species are classified into quality groups according to Šoštarić-Pisačić method [13], revised by Stavretović [6]. According to this method, all recorded plant species are classified into one of the following groups: quality grasses, bad quality grasses, leguminosae, other herbaceous plants and woody seedlings. Quality grasses are those that tolerate low mowing, resistant to pathogens, give a uniform lawn appearance, have a clear green colour precisely dark green color and completely cover the earth surface [6].

The following parameters were measured for each phytocenological record: record size (m^2), coverage (%), geographical coordinates, altitude, exposition, slope (º), height (cm), total number of species in the record. Precise coordinates and altitudes were measured using the GPS device iGO primo. Terrain exposure was determined using a compass. The assessment of the lawn quality determines the height and the coverage, which in these investigations are taken as essential quality parameters. The lawn height is determined using the instrument for measuring the height [14]. In all the phytocenological recordings/screenings, a scale for number and covering was used (Braun-Blanquet, 1928) with the following numerical marks: R (rare species), +, 1, 2, 3, 4, and 5 (the highest mark shows the greatest domination of species in regard to both traits). An analysis of the visual and functional characteristics of the lawns was made including all mentioned parameters.

RESULTS AND DISCUSSION

The researched area - “Biser” nautical village

Nautical village "Biser" is located in Boljevci, on the left bank of the Sava River, 35 km upstream from Belgrade. It is a complex of 16 modern water houses that stand in a line, looks like jewelry on the coast of the Sava river from which village name comes from [15]. The village was built in 2009 to help improvement of nautical tourism in the territory of the Surčin municipality. "Biser" is managed by Public Enterprise for performing activities in the field of sports and recreation (PE for Sport and Recreation, Surčin). Nautical village "Biser" extends on 3 hectares of green area, where plant species *Populus alba* and *Populus x euramericana* prevail. This is a great place for excursions, holidays, recreation, fishing, "team building" organization. Visitors can use volleyball courts, a bicycle path, children playground or football play on the sand. Across the river, opposite to nautical village, is a picnic area that occupies 12 hectares of forest which can be access by boat. Harbor with boat berths is of particular importance where visitors can storage their vessels even throughout the whole year (Figure 1) [15].

Figure 1 *Site display of nautical village "Biser" [3]*

Lawn structure in nautical village "Biser"

Floristic composition and lawn structure in "Biser" nautical village was researched according to 8 phytocenological records (Table 1). The total number of plant species determined in the investigated areas is 42. From the total number of registered plants 4 species are characterized as quality grasses (10%), 7 species belongs to group bad quality grasses (17%), 3 species are leguminosae (7%). More than a half recorded plant species are characterized as other herbaceous plants (59%) while 3 species are woody seedlings (Figure 2). The following species stand out with their number and cover in the group of other herbaceous plants: *Taraxacum officinale* (L.) Weber ex F.H. Wigg, *Glecoma hederacea* L. and *Ajuga reptans* L. Plants *Taraxacum officinale* (L.) Weber ex F.H. Wigg and *Cynodon dactylon* (L.) Pers. are the species recorded in all phytocenological records while *Cynodon dactylon* (L.) Pers. and *Trifolium repens* L. stand out with high number and cover in almost all records. *Cynodon dactylon* (L.) Pers. shows the ability to easily occupy the area suppressing other species especially on compact and warm habitats and survives in very unfavorable environmental conditions also [16]. *Trifolium repens* L. probably due to its growth morphology is the plant very good ajusted to the conditions of intense trampling [16], which are also conditions prevail in the area of "Biser" nautical village.

Investigated grasslands are characterized by low aesthetic value, indicated by the results of the lawn structure. Results indicate that law care and maintenance at research site are absent or inadequately and timely carried out. The results of lawn structure analysis are in agreement with the research of lawns structure in recreational areas in Belgrade [6,16], and in Serbia also [17,18]. A large percentage share of bad quality grasses (17%) shows low care and maintenance of lawn area in "Biser" nautical village. However, four species belonging to a group of bad quality grasses (*Sorghum halepense* (L.) Pers., *Bromus mollis* L., *Hordeum murinum* L. and *Dactylis glomerata* L.) are present with low values of measured parameters

(R or +), and would be easy to remove them from the green areas using an adequate program of care and maintenance. This is especially important because these species belong to the category of allergenic grasses [19].

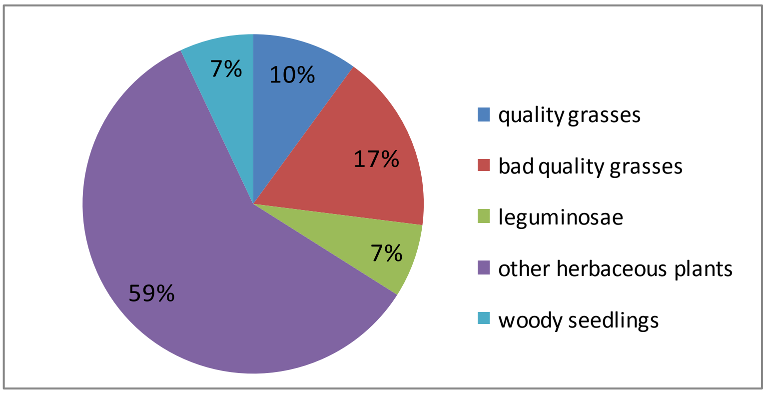

Figure 2 *The presence of plant species according to quality groups on the lawns in "Biser" nautical village*

Size of phytocenological records range from min. 20 m^2 to max. 50 m^2 while plant coverage in the surveyed areas was in the interval from 10% to 90%. The largest lawn coverage was recorded on a slope along the coast of the Sava River (P2). This area characterized by the largest number of plant species in the record which is most likely the result of a favorable exposure (NE), the exposure to users (proximity to restaurants) but also the influence of the Sava River on plants heterogeneity. The presence of watercourse and higher frequencies of visitors leads to an increase in the floristic diversity of the recreational area [7]. The average lawns height on the analyzed areas is 6 cm, and the highest height is recorded on a surface on a slope along the Sava River (P2). The highest lawn height on a slope along the river Sava points to a different way of maintenance, i.e., the frequency of mowing the coastline compared to other surfaces in nautical village. The application frequency of lawn care and maintenance measures needs to be the same throughout the whole area of "Biser" nautical village. This is especially important in the coastal zone, where a large number of visitors of the area are concentrated due to the existence of users facilities.

Table 1 *Phytocenological records of lawn in "Biser" nautical village*

Record No	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**
Size (m^2)	20	20	50	50	50	20	50	10
Coverage (%)	70	90	10	15	60	80	80	70
Geographical coordinates	N 44° 42’ 59” E 020° 13’27”	N 44° 42’59” E 020° 13’27”	N 44° 43’ 00” E 020° 13’25”	N 44° 42’59” E 020° 13’23”	N 44° 42’59” E 020° 13’27”	N 44° 42’ 59” E 020° 13’29”	N 44° 43’ 00” E 020° 13’30”	N 44° 43’ 00” E 020° 13’31”
Elevation (m)	97	94	97	97	97	97	90	89
Slope (°)	/	35	/	/	/	/	/	/
Exposition	NE	NE	NE	NE	NE	NE	NE	NE
Hight (cm)	6	20	5	5	5	6	7	7
No of species in record	19	22	10	11	8	16	12	21
Quality grasses:								
Species name								
1. *Lolium perenne* L.	+				2.2	2.2	2.2	2.2
2. *Festuca rubra* L.	R	R				R		
3. *Poa trivialis* L.								+
4. *Poa nemoralis* L.		R						

Bad quality grasses:								
1. *Cynodon dactylon* (L.) Pers.	2.2	2.2	R	R	R	2.2	2.2	2.2
2. *Poa annua* L.	1.2		R		R	R	R	
3. *Agropyron repens* (L.) Beauv.		3.2		R		1.2		
4. *Sorghum halepense* (L.) Pers.		1.1						
5. *Bromus mollis* L.				R				
6. *Hordeum murinum* L.			R					
7. *Dactylis glomerata* L.								R
Leguminosae:								
1. *Trifolium repens* L.	2.3	2.3	R	R	3.3	2.3	1.3	R
2. *Vicia cracca* L.	R	R	R					R
3. *Medicago lupulina* L.	+							+
Other herbaceous plant:								
1. *Taraxacum officinale* (L.) Weber ex F.H. Wigg	2.2	1.2	R	R	R	2.2	2.2	3.2
2. *Polygonum aviculare* L.	R	+	1.1	1.1		R		R
3. *Plantago major* L.	R	R		R	+	+	+	+
4. *Glecoma hederacea* L.	2.3					2.3	+	
5. *Ajuga reptans* L.		2.2						
6. *Stellaria media* (L.) Vill.			+	1.1			+	
7. *Convolvulus arvensis* L.	+	+						1.1
8. *Plantago media* L.	1.1					+	+	
9. *Stenactis annua* (L.) Nees.						+	+	+
10. *Plantago lanceolata* L.	R				R		+	+
11. *Calystegia sepium* (L.) R. Br.		+				+		
12. *Verbena officinalis* L.		+						+
13. *Latuca serriola* L.								+
14. *Lamium purpureum* L.	R	R						
15. *Oxalis acetosella* L.	R					R		
16. *Erigeron canadensis* L.	R	R		R				
17. *Rorippa sylvestris* (L.) Bess.		R		R				
18. *Ranunculus repens* L.		R						
19. *Bellis perennis* L.		R				R		
20. *Capsella bursa pastoris* (L.) Medik.			R	R				
21. *Rumex obtusifolius* L.					R			
22. *Aster lanceolatus* Willd.								R
23. *Achillea millefolium* L.								R
24. *Carex hirta* L.								R
25. *Geum urbanum* L.								R
Woody seedlings:								
1. *Populus alba* L.	+	R	R			R	R	R
2. *Robinia pseudoacacia* L.	R	R						
3. *Rubus caesius* L.		R						R

CONCLUSION

The results will contribute to proposing measures for planning, lawn care and maintenance of green areas in "Biser" nautical village. The largest number of recorded plants belongs to a group of other herbaceous plants which participate in the lawn structure with 59%. On the entire area much smaller number of plants belonging to the category of high-quality grasses was determined. The highest lawn coverage, average height and number of plant species is observed on a slope along the coast of the Sava River, which is the consequence of extensive lawn care and maintenance measures. Due to the existence of users facilities along the coast of the Sava river, a large number of visitors are concentrated, so lawn care and maintenance needs to be intensified and carried out properly and timely. Urban lawns are subject to changes due to the weeds occurrence, diseases, insect attacks or other factors. Lawn structure analysis points out on the low level of lawn care and maintenance of researched area.

In general the results of lawn structure analysis indicated some of the basic care measures that has to be implemented on area: regular mowing of lawns to reduce the presence and spread of weeds, removal of mowed grass, grabbing lawns, aerification as needed, lawn overseeding with adequate seed mixture (quality plant species suitable for proper type of lawns), regular applaying organic and mineral fertilizers, irrigation as needed and depending on the type of lawns, controlling weeds, pests and diseases.

The lawns in nautical village "Biser" intended for recreational activities and children's play and have decorative significance on the other side requires the following measures of care and maintenance: overseeding with quality plant species seed mixture, aerification, fertilization, soil grading as needed and regular mowing in order to reduced the presence and further expansion of weeds. The lawn on the slope along the Sava River should be maintained with the application of following maintenance measures: resowing with high-quality plant species that directly allow substrate stability and regular mowing to reduce the presence and further spread of weeds. Lawn care and maintenance should be planned depending on the type of lawns. They must be done professionally, correctly and timely. An analysis of the lawn structure in nautical village "Biser" in Boljevci was of great importance for the improvement of the entire green area and the further development of nautical tourism in the territory of Surčin municipality and the city of Belgrade.

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EXPENDITURE ANALYSIS OF PUBLIC URBAN LAWNS MAINTENANCE IN BELGRADE

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Abstract

Urban green areas management is very complex and diverse, so it's handed to firms with competent professional personnel. Green areas play a very important role in Belgrade's landscape and the lawns in them are a basis on which all other elements are "diminished". Today lawns are the most frequently maintained element in urban landscape and financial funds needed to fulfill the basic functions and purposes are great. Main goal of this paper is to analyze and display financial funds distribution of public urban lawns maintenance in Belgrade. Paper analyze the participation of lawns maintenance costs in relation to the total annual costs of maintaining green areas. Data was analyze over 10 municipalities in Belgrade covers three year span (2010, 2012. and 2015.). Results have shown that significant part of the total funds stands out for operations concerning lawn care and maintenance (44-53%). There are big differences in the distribution of financial funds regarding lawn maintenance and the value of lawn maintenance costs per unit area between central city municipalities (Stari Grad, Vračar) and district Novi Beograd for the entire research period. Obtained results are of great importance for future analyzes and planning related to structure and functioning of public green spaces of Belgrade from a standpoint of quality and sustainable development. The results provide an insight into the real costs of green area development and management of extremely important infrastructure branch of the modern city such as Belgrade.

Keywords: Lawns, Urban greening, Lawn care and maintenance, Green area management

INTRODUCTION

Urban green areas (UGA) have exceptional significance and great impact on the life quality of urban residents. The most important are sanitary, aesthetic, engineering-technical and architectural- urban functions of urban greenery [1]. An adequate organizing, management and maintaining of UGA, their accessibility and enabling of ecologically based comfort, all contribute to the functional and spatial unity of ambiance [2]. Greatest value of UGA is their vegetation consisted of trees, shrubs, flowers and other surface vegetations [3]. Greenery in these spaces, an organic component of the city, together with the complex of objects, creates the image of city landscape [4]. Lawns of green spaces represent a foundation where all other elements are being laid, or an effective final layer of a green space [5], as well as standalone green space [6,7]. The total grassland area in each country is enormous, and due to size and rapid urbanization, the scientific study of urban lawns is in expanding [8-10]. Performance of UGA is very complex and diverse [11], so it's handed to firms with competent professional personnel who, above all, include landscape architecture engineers [4]. Green areas in the city are a part of the city's communal system [12]. Today lawns are the most intensively maintained ecosystem in the urban landscape related to large annual monetary value of services and products [13,14].

Belgrade is the capitol and the biggest city in republic of Serbia and managing its UGA represents particular challenge, not just in terms of size and scope, but also because of distinct socioeconomic state of society [4]. Public utility enterprise (PUC) "Zelenilo – Beograd" supervises capitol's green spaces. Under company's management is approximately 3,000 hectare of urban open spaces (parks, squares, recreational complexes, green residential areas, street lawns etc.) [15]. Annual budget size for UGA of Belgrade is, in all account, defined in advance by Belgrade city consul's decision. It is of great practical importance to further analyze such large company's allocation method of designated funds. This paper's goal is to give insight and to analyze financial funds distributions of public urban lawns maintenance in Belgrade. Financial funds distribution analysis collected data by 10 Belgrade districts during three calendar years. Also, the paper analyze the share of the financial funds distributions of public urban lawns maintenance in relation to total annual funds of maintaining green areas of Belgrade.

MATERIALS AND METHODS

Public green spaces are an integral part of Belgrade, the capital of the Republic of Serbia, where 1,659,440 permanent residents live [16]. The area of the city of Belgrade occupies 322.268 ha (narrowly urban area extends to 35.996 ha) [16]. Inner city territory of Belgrade spans over 10 districts with total area of 103.196 ha [4]: Stari Grad, Palilula, Vračar, Zvezdara, Savski venac, Voždovac, Rakovica, Čukarica, Zemun and Novi Beograd . This 10 district form a city core, therefore lawns of public UGA in these districts are selected to be subject of this paper.

Financial funds distribution analysis of public urban lawn care and maintenance for city of Belgrade is done by using data collected from PUC "Zelenilo-Beograd", Urban open space maintenance sector's annual reports. Expenditure analyses of public lawn maintenance covers three year span (2010, 2012 and 2015). Observation was made twofold: through financial report and work actualization report which are illustrated through area size of these green spaces. Data are sorted over 2 categories: 1. operation and numerous types of elements related to lawn establishment and maintenance and 2. other operation and elements.

In data interpretation, the implemented size was used - the monetary value of lawn maintenance per unit area, expressed in the unit rsd / m^2 ("maintenance costs per square meter"), in order to obtain comparative comparisons in the various municipalities of Belgrade. "Maintenance costs per square meter" is a derivative unit which helps to conclude about the type of urban lawns as well as the average city-wide trend. The trend of financial funds distribution was also analyzed in relation to the total funds allocated to municipalities. Financial funds distribution analysis related to the dynamics of the lawn maintenance operations throughout the year, shows the real significance of the lawn as an element of the urban landscape of Belgrade. The obtained results are significance for future planning in order to develop the quality green infrastructure, right functioning of the city of Belgrade and sustainable development of its green areas. Also, the results provide an insight into the inevitable costs of developing this extremely important branch of the infrastructure of a modern city, whose status Belgrade certainly deserves due to its role and size.

RESULTS AND DISCUSSION

In year 2010 total annual budget allocated and realized for management of urban green area under jurisdiction of PUC "Zelenilo-Beograd" amounts 1.017.797.705 dinars (table 1) while lawn establishment and maintenance operations receives 538.360.672,53 dinars (53%).

In year 2012 little bit less than a half of total annual budget allocated and realized for management of UGA goes to category lawn establishment and maintained (44%). According to realization work financial report for year 2015, annual budget for management of urban open spaces under jurisdiction of PUC "Zelenilo-Beograd" sum of total funds allocated for this purpose is 1.251.915.971 dinars while percentage share of costs that goes to the lawn maintenance operations is 47%.

Table 1 *Total financial funds distribution for the city of Belgrade over three year span*

	BELGRADE		
	year 2010	year 2012	year 2015
LAWNS MAINTENANCE (rsd)	538,360,672.53	550,089,723.12	592,024,732.69
OTHER (rsd)	479,437,033	685,938,698	659,891,239
TOTAL (rsd)	**1,017,797,705**	**1,236,028,421**	**1,251,915,971**

Total financial funds distribution analysis of public urban green areas maintenance in Belgrade shows that significant percentage share part of the funds is allocated for lawn maintenance operations (44-53%). Under the category "other" are all operations related to flowers, perennials and roses, hedge and shrubs, trees, hygiene, park accessories, etc.

Table 2 *Lawn maintenance financial funds distribution (rsd) in 10 Belgrade municipalities over three year span*

TOWN DISTRICT	Year 2010.	Year 2012.	Year 2015.
STARI GRAD	22,357,033.02 rsd	19,743,877.40 rsd	15,002,224.08 rsd
PALILULA	43,266,477.80 rsd	45,282,188.91 rsd	55,322,980.36 rsd
VRAČAR	12,659,046.78 rsd	16,434,820.23 rsd	15,952,843.41 rsd
ZVEZDARA	37,990,691.16 rsd	38,885,227.36 rsd	40,679,961.13 rsd
SAVSKI VENAC	38,159,376.61 rsd	34,282,394.32 rsd	49,692,647.76 rsd
VOŽDOVAC	45,599,993.90 rsd	45,163,239.36 rsd	64,547,332.70 rsd
RAKOVICA	60,717,607.36 rsd	56,226,894.90 rsd	62,620,235.55 rsd
ČUKARICA	55,041,639.84 rsd	62,588,843.70 rsd	58,162,767.47 rsd
ZEMUN	41,860,694.72 rsd	45,186,717.10 rsd	46,072,239.20 rsd
NOVI BEOGRAD	180,708,111.34 rsd	186,295,519.84 rsd	183,971,501.03 rsd

According to lawn maintenance financial funds distribution for the city of Belgrade for researched period, the lowest total financial funds is realized for districts Vračar and Stari Grad (Table 2). The most finances were allocated to the municipality of Novi Beograd. This is related to the lawn size in these municipalities (Table 3), green areas structure, basic purpose and functions of UGA. Vračar and Stari Grad are the smallest municipalities by size. As an older municipalities they went through different stages of development, but always remained central municipalities very important for the town functioning and cityscape. With compact phisical structure central municipalities are densely populated, with numerous administrative centers and institutions, which led to the development of green spaces more in aesthetic and representative than in a functional direction. Therefore, the lawns within the green areas of the municipalities of Vračar and Stari Grad are reduced to a small size with a maintenance at a high level.

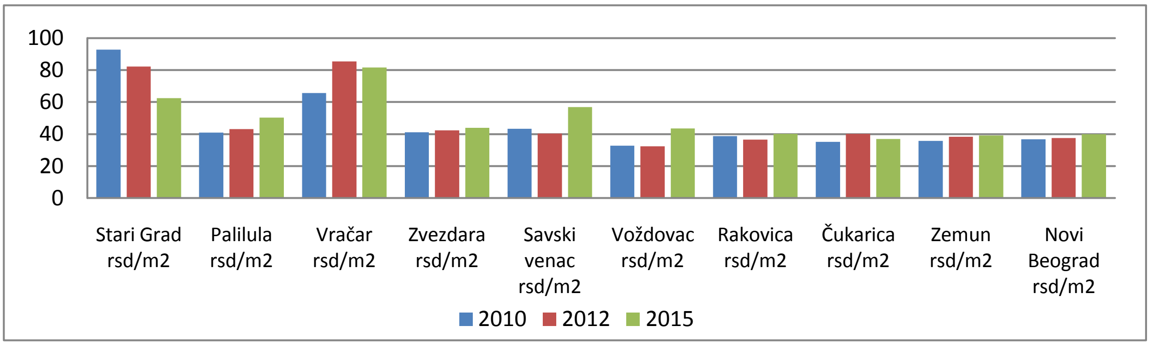

Figure 1 *Costs of pubic lawn "maintenance per unit area" (rsd/m^2) in 10 Belgrade municipalities over three year span*

The research results indicate the highest lawn maintenance costs per unit area in municipalities Stari Grad and Vračar (Figure 1). The highest level of lawn maintenance is precisely in the area of central city municipalities with an average price twice higher than the average for Belgrade (Table 3). This high price of lawn maintenance is a result of very small but high quality green areas in central municipalities, where lawns are standelone in the parterre or present like (high) decorative in parks or a part of specially decorated spaces. There is a completely different situation in the municipality of Novi Beograd. Novi Beograd municipality is a young one, a territorially large, structurally formed and defined since the beginning of its existence. From an urbanism point of view, there is clearly resolved residential and industrial zones, with rationally integrated green areas of various functions, focused primarily on users and sanitary-protection. In this type of municipality, lawns in urban greenery easily exceed all other structural elements. The cause of lawn domination is first of all functional (living space, various forms of protection, etc.), and then aesthetically. Eventhough Novi Beograd has approximately 22.5 times larger lawn areas than other municipalities in Belgrade this district succeeded to maintain the lowest price of grassland care, far below the Belgrade average (32.46 din/m^2) (Table 3). This is primarily attributed to planning construction of green areas with the aim of easier maintenance and greater savings.

Lawns are the dominant element of urban green areas in all 10 municipalities in Belgrade and more detailed analysis of these structures is of great importance. The diversity and different purposes of public urban lawns in Belgrade requires special attention regarding current state and forming a detailed picture of the functioning of these structural elements of green areas.

Table 3 *Total lawn area and maintenance costs per unit area in 10 Belgrade municipalities over three year span*

Municipality	unit measure	Year 2010.	Year 2012.	Year 2015.
Stari Grad	m^2	240,782.00	240,267.00	240,411.00
	rsd/m^2	92.85	82.17	62.40
Palilula	m^2	1,057,359.10	1,052,186.00	1,102,051.30
	rsd/m^2	40.92	43.04	50.20
Vračar	m^2	192,583.00	192,419.00	195,334.03
	rsd/m^2	65.73	85.41	81.67
Zvezdara	m^2	925,648.35	920,658.35	925,014.65
	rsd/m^2	41.04	42.24	43.98
Savski venac	m^2	882,459.20	850,831.20	873,536.54
	rsd/m^2	43.24	40.29	56.89
Voždovac	m^2	1,393,245.96	1,393,403.00	1,480,685.00
	rsd/m^2	32.73	32.41	43.59
Rakovica	m^2	1,569,836.00	1,536,331.00	1,560,879.30
	rsd/m^2	38.68	36.60	40.12
Čukarica	m^2	1,567,223.00	1,557,754.00	1,573,799.00
	rsd/m^2	35.12	40.18	36.96
Zemun	m^2	1,173,793.00	1,177,477.00	1,180,505.00
	rsd/m^2	35.66	38.38	39.03
Novi Beograd	m^2	5,687,451.00	5,710,409.00	5,667,171.60
	rsd/m^2	31.77	32.62	32.46
TOTAL (Belgrade)	m^2	14,690,380.61	14,631,735.55	14,799,387.42
	rsd/m^2	36.65	37.60	40.00

CONCLUSION

Continuous monitoring, prevention, problem detection and timely interventions of everyday issues concerning UGA management are necessary in every capital city. Expenditure analysis of public urban green areas maintenance in 10 Belgrade municipalities have shown that significant amount of funds are allocated for lawn. Also, there are different approaches to maintaining green areas in 10 city municipalities which can be seen through examples of Novi Beograd and Stari Grad municipalities. It could be noted that each municipality has specific requirements and priorities related to urban greenery. Each town district has special maintenance programs that are formed according to number of individual factors and circumstances during the season.

Results indicate Stari Grad and Novi Beograd like two opposite municipalities regarding urban greenery maintenance. Stari Grad forms a narrow city core, its structure and development go hundreds of years in the history of Belgrade and follow all its time periods. Landscape uiformity in Novi Beograd area has been broken up by green formations, diversity in plant selection, their space arrangement and the overall content and atmosphere of the natural environment providing spaces for playing, socializing and escaping from the city's everyday life. Lawns of Novi Beograd and its spatial distribution, beside the physical environment have a significant psychological role, because they offer openness and color contrast to an environment that would otherwise be dense and overcrowded.

Lawns in the Belgrade greenery play an important role, primarily as a high percent share of green areas, as well as the financial funds that are allocated at the city level for their formation and maintenance. Lawn appearance and functioning depend on a number of factors, while construction and maintenance cost depends largely on the quality that lawns should have in accordance with achieved functions. Lawns are the most dynamic element of urban greenery and represent areas where inadequate or poor maintenance are the most rapidly visible changes. Public urban lawns require constant monitoring as well as constant maintenance and protection measures.

Whether the existing maintenance measures will be sufficient under some small changes or it will be necessary to introduce some radical changes in the technique of maintaining lawns and green areas in its entirety, the task is for future research.

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HEALTH ASPECTS OF THE INDOOR CONDITIONS (REVIEW)

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Abstract
Up to 80-90% of the day time the residents of developed countries are spending in a residential and business indoor environment, the most of it in the apartments [2]. Therefore, the impact of indoor conditions on human health is very high, and is especially important for the most vulnerable part of the population (chronic patients, children and old people, handicapped). Indoor conditions are one of the most important factors that can lead to health disorders due to exposure to harmful factors, including chemicals, moisture and mould, noise, radon, pests and microorganisms, injuries. The aim of this review is to point out the most important health risks connected with indoor conditions.

Keywords: Indoor conditions, Health, Risk

INTRODUCTION

As early as 1938, the Committee for housing hygiene of the American public health association (APHHA), gave the basic principles of healthy living as a guide to meeting the basic needs of people related to housing [1]. They include the basic criteria for comfortable and healthy living, as well as physiological and psychological needs.

Under the basic physiological needs in this context, the following are assumed:

- Protection from bad weather conditions,
- A thermal environment that will prevent unnecessary loss of heat and will enable the necessary loss of body heat,
- Adequate air purity,
- Adequate daily and artificial illumination,
- Protection against excessive noise and
- Providing adequate space for physical activity and children's play.

Basic psychological needs are met if the following is provided:

- Adequate privacy,
- Conditions for normal family life, as well as for community life,
- Technical conditions that enable the performance of household work without unnecessary physical and mental fatigue,
- Technical possibilities for maintaining personal and space hygiene,
- Satisfaction of aesthetic needs in the apartment and environment and
- Compliance with the dominant social standard of the local community.

From the defined needs, it is clear that the provision of healthy living, based on public health principles, is much more than satisfying technical standards, engineering and aesthetic solutions.

THE MOST IMPORTANT HEALTH DISORDERS CONNECTED WITH INDOOR CONDITIONS

Injuries - The injuries of different types and intensities can occur in indoor conditions. Physical injuries, from cuts and scrapes, to traumas with fatal outcomes can happen due to falls on slippery floors, poor lighting, overcrowding of the apartment, inadequate protection on windows, etc. [2]. Chemical injuries are very common for small children, mostly in contact with household chemicals. The chlorine gas is especially dangerous. It can be formed in the reaction of ammonia or acid-based preparations and chlorine bleach. Chlorine gas causes respiratory irritation. Naphthalene based anti-mothers can cause various symptoms, from headache, nausea, nausea, vomiting and diarrhoea, to anaemia, liver damage, and neurological damage in the youngest age.

Microbial agents and pests - In the second half of the 20th century, due to the improvement of living and working conditions, as well as the application of medicamentous therapy and specific immunization, there was a significant reduction of the incidence of Tuberculosis. But, in the late 20th and early 21st century, the incidence of this socio-medical illness is increasing again, both in undeveloped and in developed parts of the world. Tuberculosis has the character of a socio-medical illness because it is influenced by the nutrition quality, housing conditions, working conditions and rest regime. Smoking also significantly contributes to the occurrence of this disease in conditions of simultaneous exposure to the microbiological agent. Its course and outcome are influenced by the time of the therapy initiation and the consistency in its implementation, as well as the habits and behaviour of the patient and his socio-economic status. A mathematical model developed by California University specialists has shown that, if the progression of Tuberculosis continues at this pace, the number of affected people by 2050 will reach the figure of 40 million.

In damp dwellings, which include apartments where the humidity is higher than 70% and the humidity of the walls is more than 3%, the development of fungi with possible irritation of visible mucous membranes, toxic effects and allergic reactions is possible. The most common mycosis is Aspergillosis, caused by Aspergilus fumigatus, which usually grows in moist baths and can cause sudden manifestation of obstructive pulmonary disease, i.e. asthma and bronchitis.

The roosters are spider webs often present in linens, upholstered furniture and carpets. Their faeces in the form of floating particles have the potential to cause diseases: asthma, atopic dermatitis, eczema and urticaria, allergic rhinitis and conjunctivitis.

The risk for human health in flats may also be the presence of insects and rodents. Insects that are most commonly involved in transmission of the disease, whether passively transmitting the causative agent of the disease, whether actively, serving as hosts in some part of the life-cycle of the cause of the disease, are yours, fleas, stenosis, ticks, mosquitoes and flies. Droplets, mites, hardwoods and butterflies inflict great damage to the material, destroying foodstuffs, textiles and furniture.

Disinfection involves the destruction of insects using mechanical, physical, chemical and biological methods.

Mechanical methods include removal of waste, washing, cleaning, chirping, brushing, application of sticky masses in the form of tape, installation of grids, air curtains, aspirators, fans...

Ultra-sound and radio waves, infrared rays, gamma radiation, electrical energy and high and low temperatures are physical measures that can be applied.

Chemical agents used against insects can be repellents and insecticides. The organic compounds that mask the body odour and reject insects are most often used as repellents: esters, alcohols, ketones and aldehydes in the form of creams, gels, lotions. Insecticides, however, cannot have repellent properties and according to the way of penetration into the organism of the insect can be contact, digestive and respiratory agents (fumigants). In treatment of Pediculosis, Pyrethrine, a plant insecticide that is not toxic to warm-blooded animals and humans, is contraindicated in pollen-sensitive individuals or asthma patients, as it is obtained by extraction from several genera of the Pyrethrum plant. It affects insects through the digestive tract and by contact. It's toxic for spiders' predators. DDT is a contact, organochlorine insecticide, which is accumulated in the body, and has a carcinogenic potential and has been forbidden. Lindan (organochloric pediculocide and skabicide), Malathion (organophosphate contact insecticide), cyanide preparations (Zyklon B, a gas produced at the end of the nineteenth century in the USA and used for citrus trees, with inhibitory activity on the production of ATP and cell breathing) etc.

Biological methods involve human interventions in the biological cycle of insects, either by increasing the number of natural insect enemies, or by radioactive sterilization, using synthetic growth hormones that disturb the insect development cycle, etc.

Pest control is a process of destroying harmful rodents, of which the most common are black rat (Rattus Rattus), grey rat (Ratus Norvegicus) and domestic mouse (Mus Musculus). Rats and mices can be the source of infections (Pestilence, Leprosy, Salmonellosis, Trichinosis, Tularaemia, Rat bite disease), or vectors of infectious disease (Salmonellosis, Shigellosis). In addition, rodents destroy huge amounts of food - it is estimated that in the United States rats eat food worth $ 960 million during one year.

The methods for pest control can be sanitary-technical (construction of solid proof buildings, metal gratings on all openings, with concrete foundations, construction of supporting concrete walls around buildings, etc.), mechanical (mouse traps, sticky masses), physical (ultrasonic waves), chemical (rodenticides of fast and slow action), biological (activity of natural rodent enemies, with no the influence of man) and bacteriological (by the addition of bacteria or their toxins to mouse bites, which, due to the risk to human and animal health, is not recommended for the application). It is usually necessary to apply more than one measure of pest control.

Traffic noise - Noise, mostly traffic noise, is associated with many adverse health effects: ischemic heart disease and myocardial infarction, stroke, hormone-independent breast carcinoma, type 2 diabetes, obesity [3]. According to numerous epidemiological studies, there is enough evidence that the effect of a noise above 65 dB can lead to myocardial infarction [2]. The most frequent reason for the presence of the indoor noise is poor zoning of settlements and poor isolation.

Radon in the apartment - The average radioactivity originating from radon in the living space is 20-40 Bq/m^3. When the radioactivity of this colourless and odourless gas, seven times heavier than air and alpha emitters is greater than 150 Bq/m^3, it is necessary to take measures to reduce the emission: good construction with no cracks, adequate ventilation, good insulation and avoiding the coating of surfaces with natural materials that release this gas, such as marble and granite. Radon concentration in the living space may be eight times higher than in the open area, and its potential to cause lung cancer increases if exposure to this gas is associated with smoking: smokers exposed to radon activity have a 10 times greater lifetime risk of developing lungs carcinoma compared to non-smokers [2].

Passive smoking - In addition to favouring radon effects and contributing to Tuberculosis, smoking and passive smoking contribute to the development of respiratory infections and asthma, as well as damage to blood vessels in children and the occurrence of lung cancer and heart disease in adults. In addition, under the influence of tobacco smoke in passive smokers, the level of Apo lipoprotein B, which is important for the development of LDL cholesterol, the risk of miscarriage increases in women, and in children there is a decline in immunity [2].

The harmful effect of tobacco smoke can be achieved in three ways: direct inhalation at smokers, passive smoking at non-smokers, and the introduction of toxins from the precipitated smoke on the surfaces.

In order to eliminate nicotine and other chemical compounds released into the air and precipitated on the walls, the best measure is to paint the walls. If this is not possible, the walls are to be washed with a mixture of ammonia and vinegar in a ratio of 1:1, with the addition of a few drops of detergent [2].

Lead is present in paint, soil and dust, as well as in drinking water, usually as a result of the presence of old leads pipes. It can lead to cognitive, developmental, neurological, cardiovascular and other disorders in low-exposure conditions, while at higher concentrations acute poisoning may occur. According to the US Environmental Protection Agency (EPA) Standard for Ambient Air Quality of 2016, which confirmed the 2008 standard, the maximum allowed lead concentration is 0.15 $\mu g/m^3$ in total suspended particles as a quarterly average value.

Carbon monoxide poisoning is the most common household poisoning. It happens during combustion of solid fuels, oil and gas, due to malfunction or clogging of chimneys and ventilation systems, or due to poor installation or failure on solid fuel stoves, gas ovens or fireplaces. The mild forms of poisoning with this colourless gas, without odour and flavour are manifested with headaches, dizziness, and confusion. Heavy poisoning can lead to the loss of consciousness and fatal outcome.

Formaldehyde - The presence of formaldehyde, gas with a specific odour, in indoor conditions is a consequence of the use of materials with a significant content of this compound: crushed wood (chipboard and plywood), some cleaning agents, paper, insulating materials, varnishes, textile products, softeners, electrical appliances, such as computers and photocopiers etc. [4]. In products made of crushed wood, formaldehyde is used as a binder (phenol-formaldehyde resins), and its release into the air of indoor space depends on the conditions of the environment: air humidity, temperature, ventilation, as well as the characteristics of the material itself: its humidity, the type and content of binders and other materials. It can be reduced by so called. "refinement of plates", i.e. their coating with different types of foils and laminates, or coating with the water based coats [4]. Formaldehyde acts as irritant, causing breathing disorders, vomiting, various allergic reactions, and belongs to a group of proven carcinogens.

"Stinky buildings" case - Based on the complaint of the tenants of the new settlement "Ivo Lola Ribar" in New Belgrade for the presence of smell in certain apartments, the experts of the Institute of Public Health of Belgrade performed measurements of the presence of pollutants in these flats, as well as in the control flats in the same settlement where the presence of smell was not detected. The results of this measurements showed the presence of phenolic substances and phenanthrene, originating from concrete as a result of coating the boards for concrete formating with oil with high content of the mentioned chemical compounds. The presence of formaldehyde in concentrations slightly larger than in the control flats was detected in the indoor air of these flats, but its presence is related to the emission charasteristic for newly constructed buildings. On the basis of the results of the conducted indoor air tests, the expert team of the Institute assessed that these new apartments do not fulfill the sanitary and hygienic standards for permanent habitation, and on that basis the Serbian Building Directorate provided the emigration and housing of the tenants of this settlement [5].

Sick building syndrome (SBS) is defined as a health disorder with non-specific subjective disorders without objective signs [6]. In this syndrome, symptoms of irritation may occur (tingling, itching and dryness of the mucous membrane of the nose, eye and throat), non-specific symptoms (headache, lethargy and concentration disturbance), skin changes (redness, dryness and itching) and, rarely, nausea, cough, hard breathing, unusual taste in the mouth All symptoms listed are benign and disappear after leaving the problematic environment The occurrence of SBS is most often noticed in new facilities with a small air cubature and new materials, “hermetically sealed”, overcrowded and often poorly maintained Agents that cause this syndrome can be physical, chemical, biological, or, most often, their combination.

Energy efficiency - One of the current topics in the field of modern housing is the topic of energy efficiency of buildings, which, in the broadest terms, touches all aspects of life in the apartment, giving the opportunity to improve every aspect, but also bearing certain risks for human health. In developed countries, energy consumption in buildings accounts for 20-40% of total energy consumption and exceeds consumption in industry and traffic in the EU and the US [7]. Energy efficiency of buildings is achieved by intervention on three levels:

1. The level of the outer shell of the building (facade, insulation, thermal breaks, carpentry).
2. The level of technical systems: mechanical (heating, cooling, air conditioning, ventilation), electrical (lighting, home appliances ...) and electromechanical systems (electric blinds, elevators...).
3. The level of automatic system management (eg activation of artificial lighting after detection of entry into the room with subsequent adjustment of the light intensity in accordance with the intensity of natural lighting, operation of low temperature heating systems, etc.).

CONCLUSION

Indoor conditions have a great public health significance, not only in terms of comfort and fulfilment of all construction and technical standards of housing, but also in terms of satisfying the physiological, psychological, social and other needs of the population, and in particular, with regard to possible health threats. Taking into account the presence of risk factors within the indoor space, the need for more intensive monitoring of harmful factors is imposed, taking preventive measures and measures for risk reduction. Also, this subject needs to be processed with an appropriate legal framework in which, among other things, the limit values for harmful and dangerous substances in the indoor space will be defined.

All previously listed health risks related to indoor conditions, which are accompanied by the mental health risks, as a very complex category, indicate that there is a need for the development of a guideline for healthy indoor environment, which will take into account, among other things, the use of new materials and measures for achieving energy efficiency, in order to ensure better control of their application.

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RADIOACTIVITY IN SOIL FROM NP DJERDAP IN 2015 AND 2016

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Abstract

In June 2015, 5 soil samples and 7 moss samples were collected from 5 locations on the territory of NP Djerdap, while in 2016 11 soil samples and 14 moss samples were collected from 8 locations. Radionuclides belonging to radioactive chains of uranium, ^{238}U, ^{226}Ra and thorium (first member ^{232}Th), the natural isotope ^{40}K, and also the artificially produced radionuclide ^{137}Cs were detected and measured in all investigated samples. The content of ^{137}Cs in moss and its substrate collected on the territory of NP Djerdap indicate that there has been no new pollution with this radionuclide on the investigated territory. The strength of the absorbed gamma radiation dose originating from the activity of radionuclides in the soil and the yearly effective dose were determined. Values of the strength of the absorbed gamma radiation dose and the yearly effective dose from external exposure to gamma radiation based on the content of natural radionuclides in soil were in the range of the expected values and close to the average values in the world.

Keywords: Radioactivity, NP Djerdap, Soil, Mosses

INTRODUCTION

The Djerdap National Park (NP) was founded in 1974. It has an area of 63680 ha. Soil is the basic natural resource in woodland ecosystems providing production and ecologic functions. It is a natural formation composed of mineral and organic components. It is divided into layers with varied thickness lying over a rocky substrate from which it differs by morphology, physical and chemical properties, biological characteristics and biological productivity. Silicate and limestone substrates are equally distributed in NP Djerdap. Brown soils (different depths) dominate on silicates or limestone [1]. During pedogenesis and evolution soil obtains certain physical properties differentiating it from the compact or loose original substrate. The water, air and heat regime of soil depends on its physical properties, influencing successful plant development and fertility. The most significant physical properties are: granulometry – mechanical composition or soil texture, specific weight, porosity, soil consistency, water and air in the soil and thermal properties with the heat regime. Some classify soil radioactivity into this group of properties, as soil represents a reservoir of not only metals, but radionuclides [2]. Radioactivity and ionizing radiation are a constant and natural quality of the environment. There are many natural radionuclides. Some long living ones exist since the formation of earth, while some are constantly created. In the

Earth crust ^{87}Rb is the most abundant natural radionuclide, followed by ^{232}Th, ^{40}K and ^{238}U. Uranium, thorium and descendants of their radioactive decay are the most significant radionuclides in the Earth crust. In nature uranium is found as a mixture of three long life isotopes: ^{238}U (99.28%; physical half-life $T_{1/2}=4.5\cdot10^{9}$ years), ^{235}U (0.71%; $T_{1/2}=7.1\cdot10^{8}$ years) and ^{234}U (0,006%; $T_{1/2}=2.5\cdot10^{5}$ years). Two types of uranium exist: inert (97% of total uranium, does not migrate through the biosphere) and mobile (0.1-3.0%, has significant ecological and biological impact, as it can transfer from soil to plants by the ion exchange process or in the form of complex compounds with organic acids from the root system). The average content of ^{238}U in soil in the world is 35 Bq/kg (span 16-110 Bq/kg) [3]. Radium-226 forms by radioactive decay of ^{238}U. It is present in different concentrations in almost all types of rock and soil that contain natural uranium. The biological significance of ^{226}Ra is based on the fact that it is a long-life radionuclide ($T_{1/2}$=1622 years) that follows calcium in the organism. It is one of the most toxic radionuclides with expressed carcinogen influence. The average content of ^{226}Ra in soil in the world is 35 Bq/kg (span 17-60 Bq/kg) [3]. Two thorium isotopes are also present in soil ^{232}Th ($T_{1/2}=1.4\cdot10^{10}$ years) and ^{228}Th ($T_{1/2}$=1.9 years). Insolubility and small content of thorium results in a small representation in the biosphere, and thus small ecological significance. The average content of ^{232}Th in soil in the world is 30 Bq/kg (span 11-64 Bq/kg) [3]. Potassium-40 is a primordial natural radionuclide with a long half-life of $1.25\text{x}10^{9}$ years. Potassium is a monovalent lithophile element under natural conditions. In nature, ^{40}K is found in a mixture with stable potassium isotopes ^{39}K and ^{41}K (^{39}K-93.08%, ^{40}K-0.1119% and ^{41}K-6.9%). Among the naturally occurring primordial radionuclides, ^{40}K ($T_{1/2}=1.28\cdot10^{9}$ y) is very abundant in soil, as the molar fraction of ^{40}K is 0.0117. In a living organism, potassium is evenly distributed. Potassium is a chemical analogue to Cesium. Among natural radionuclides, only ^{40}K is considered essential as it is part of the human organism and is under homeostatic control. The average specific activity of ^{40}K in soil in the world is 400 Bq/kg (span 140-850 Bq/kg) [3]. With his activity, man has produced new sources of ionizing radiation. Radiocesium ^{137}Cs is one of the most dangerous released radionuclides for organisms. It can form as a fission product, produced in the process of production and testing of nuclear weapons and in nuclear reactors. Radiocesium most often reaches organisms by dry or wet precipitation. Adoption of cesium from the environment can be: physical and chemical sorption and ion exchange. It has a long half-life (30.2 years). Its physico-chemical characteristics are such that it actively participates in the food chain of humans and animals through plants, as it metabolically replaces potassium. It is completely soluble in body fluids and is evenly distributed in the organism. A critical organ does not exist for ^{137}Cs as it is an organotropic radionuclide. A large amount of radionuclides was released into the atmosphere with the Chernobyl accident (26.04.1986, Ukraine) of which $3.7\text{x}10^{16}$ Bq of ^{137}Cs. There was no significant deposition of this radionuclide in Serbia after the accident in the Fukushima nuclear power plant in 2011 [4].

MATERIALS AND METHODS

Investigations performed on the territory of NP Djerdap in the last few years have shown that the radionuclide content in moss and its substrate is not homogenous and this is the reason why mosses and substrates were collected from previously defined locations. In June 2015 5 soil samples and 7 moss samples were collected from 5 locations in NP Djerdap, while in June 2016 11 soil samples and 14 moss samples were collected from 8 locations. In the laboratory the samples were cleaned from visible impurities (soil, grass, pine needles) dries, homogenized and packed in Marinelli vessels with a volume of 1L. They were sealed with paraffin and left for at least four weeks to establish a radioactive balance between ^{226}Ra, ^{222}Rn and their short-life descendants. Moss sample mass was up to 100 g, and the substrate was up to 500 g. A semiconducting germanium high purity detector 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 detection. The Department of Physics, Faculty of Natural Sciences University of Novi Sad performed calibration of the detector efficiency and energy. All samples were measured for 60000 s. The ^{238}U content was determined based on gamma lines: ^{234}Th (63 and 93 keV) and ^{234}Pa (1001 keV). The ^{226}Ra content was determined based on gamma lines: ^{214}Bi (609, 1120 and 1764 keV) and ^{214}Pb (295 and 352 keV). The ^{232}Th content was determined based on gamma lines ^{228}Ac (338, 911 and 969 keV). The ^{40}K content was determined based on the gamma line at 1460 keV, and ^{137}Cs based on the gamma line at 661.6 keV. Spectra were analyzed using the Gamma Vision 32 software package. The relative measuring error of sample preparation and measurement was up to 10%.

RESULTS AND DISCUSSION

The results obtained from measuring the content of radionuclides in investigated soil and moss samples collected in 2015 on the territory of NP Djerdap, including values of the absorbed radiation dose D (nGyh^{-1}) and yearly effective dose D_E (mSv) are given in Table 1.

Table 1 *Radionuclide content (Bq/kg) in soil and moss samples collected in 2015 in NP Djerdap and also values of the absorbed radiation dose D (nGyh^{-1}) and yearly effective dose D_E* (mSv)

Locality	**Sample**	**^{137}Cs**	**^{40}K**	**^{226}Ra**	**^{232}Th**	**^{238}U**	**D**	**D_E**
		(Bq/kg)					**(nGyh^{-1})**	**(mSv)**
1	Soil	36.0	145	5.8	4.8	6.8	11.6	0.014
	Moss1	38.0	153	5.2	4.4	17.2	---	---
2	Soil	130	597	42.8	34.2	33.3	65.3	0.080
	Moss 1	39.0	229	12.9	9.3	13.3	---	---
3	Soil	92.1	132	4.9	4.1	3.6	9.8	0.029
	Moss 2	50.0	153	4.3	5.2	18.6	---	---
4	Soil	632	441	4.6	5.2	5.1	23.7	0.029
	Moss 1	512	192	16.7	19.3	4.3	---	---
5	Soil	205	660	32.9	46.0	26.5	70.5	0.087
	Moss 2	230	156	8.4	8.8	15.5	---	---
	Moss 1	503	237	14.7	20.2	24.3	---	---
	Moss 3	303	210	7.6	7.8	27.0	---	---

Soil and moss samples were collected from the following locations: 1. Desna river, 47/a; 2. Boljetin river, 9/c; 3. Poreč wood, 60; 4. Djerdap, 78f; 5: Crni vrh. Moss samples were: 1. *Polytrichum formosum* Hedw.; 2. *Hypnum cupressiforme* Hedw.; 3. *Kindbergia praelonga* (Hedw.) Ochyra. The average value (Bq/kg) of the radionuclide content in soil collected in 2015 was: ^{137}Cs 219, ^{40}K 395, ^{226}Ra 18.2, ^{232}Th 18.9 and ^{238}U 15.1 that is within the range of average values in soil in the world [3]. In moss it was: ^{137}Cs 239, ^{40}K 190, ^{226}Ra 10.0, ^{232}Th 10.7 and ^{238}U 17.2 that is in the range determined in our previous research [5]. The radionuclide content (Bq/kg) in soil (moss) was: ^{137}Cs 36.0-632 (38.0-512), ^{40}K 132-660 (153-237), ^{226}Ra 4.6-42.8 (4.3-16.7), ^{232}Th 4.1-46.0 (4.4-20.2), ^{238}U 3.6-33.3 (4.3-27.0). The results obtained from measuring the radionuclide content in investigated moss and soil samples collected in 2016 on the territory of NP Djerdap, and also values of the absorbed radiation dose D (nGyh^{-1}) and yearly effective dose D_E (mSv) are given in Table 2. Soil and moss were collected from the following locations (state unit- GJ, department): 1. Crni vrh, 54;

2. Crni vrh, 4; 3. Crni vrh, 59; 4. Crni vrh, 13; 5. Leva reka, 27; 6. Boljetinka, 81; 7. Boljetinka, 58; 8. Boljetinka, 66. Moss samples were: 1. *H. cupressiforme* Hedw.; 2. *P. formosum* Hedw.; 3. *Brachythecium rutabulum* (Hedw.) Schimp.

Table 2 *Radionuclide content (Bq/kg) in soil and moss samples collected in 2016 in NP Djerdap and also values of the absorbed radiation dose D (nGyh^{-1}) and yearly effective dose D_E (mSv)*

Locality	Sample	^{137}Cs	^{40}K	^{226}Ra	^{232}Th	^{238}U	D	D_E
				(Bq/kg)			(nGyh^{-1})	(mSv)
1	Soil	490	535	37.2	44.3	48.6	66.3	0.081
	Moss1	138	100	19.3	9.2	18.2	---	---
	Moss2	84.4	267	27.0	12.2	26.4	---	---
2	Soil	102	471	25.0	32.1	20.6	50.6	0.062
	Moss2	105	131	4.2	5.1	12.4	---	---
	Soil	333	621	16.3	22.1	20.9	46.8	0.057
	Moss2	90.9	251	12.7	8.9	35.5	---	---
3	Soil	107	468	12.1	15.0	11.4	34.2	0.042
	Moss2	28.2	218	6.9	3.6	7.9	---	---
4	Soil	104	456	37.3	35.7	46.5	57.8	0.071
	Moss2	95.7	247	16.5	12.1	16.7	---	---
5	Soil	28.7	63.1	1.8	1.9	1.5	4.6	0.006
	Moss2	57.2	213	6.9	7.0	12.9	---	---
6	Soil	491	332	22.9	23.9	17.2	38.9	0.048
	Moss1	101	19.0	18.1	7.4	16.5	---	---
	Soil	353	309	21.7	20.0	22.8	35.0	0,043
	Moss1	139	171	5.0	8.2	12.2	---	---
	Moss2	180	198	11.2	14.0	25.4	---	---
7	Soil	38.6	200	20.8	18.1	11.4	28.9	0.035
	Moss2	38.5	273	26.9	25.5	55.2	---	---
8	Soil	72.2	335	15.4	15.2	14.9	30.3	0.037
	Moss2	72.2	293	21.6	10.5	21.4	---	---
	Moss2	42.5	282	10.6	8.2	27.7	---	---
	Soil	55.7	363	13.9	15.5	17.8	30.9	0.038
	Moss3	54.9	237	12.0	20.2	24.0	---	---

The average radionuclide content (Bq/kg) in soil collected in 2016 was: ^{137}Cs 198, ^{40}K 378, ^{226}Ra 20.4, ^{232}Th 22.2 and ^{238}U 21.2 that is within the range of average values in soil in the world [3] and moss was: ^{137}Cs 87.7, ^{40}K 207, ^{226}Ra 14.2, ^{232}Th 10.9 and ^{238}U 22.3 that is in the range determined in our previous research [5]. The content (Bq/kg) in soil (moss) collected in NP Djerdap in 2016 was: ^{137}Cs 28.7-491 (28.2-180), ^{40}K 63.1-621 (19-293), ^{226}Ra 1.8-37.3 (4.2-27.0), ^{232}Th 1.9-44.3 (3.6-25.5), ^{238}U 1.5-48.6 (7.9-55.2). The measured values for the content of radionuclides with a natural origin are within the world average content range [3]. The calculated values of the Pearson correlation coefficient for radionuclides in soil collected in 2015 and 2016 on the territory of NP Djerdap show a strong correlation between ^{40}K and the other natural radionuclides. The strength of the absorbed dose of gamma radiation originating from activity of radionuclides in soil can be calculated using the following equation:

$$D(\text{nGyh}^{-1}) = 0.462 x C_{Ra} + 0.604 x C_{Th} + 0.0417 x C_K \quad (1)$$

where C_{Ra}, C_{Th}, C_K are the radionuclide content in soil, while according to recommendations of UNSCEAR, corresponding conversion coefficients are: 0.462 nGy h^{-1}/(Bq kg^{-1}), 0.604 nGy h^{-1}/(Bq kg^{-1}), 0.0417 nGy h^{-1}/(Bq kg^{-1}), respectively [3,6]. The strength of the absorbed gamma radiation dose (nGy/h) in 2015 on the territory of NP Djerdap is in the range from 9.8 to 70.5, while in 2016 it was from 4.6 to 66.3. The yearly effective dose was determined as:

$$D_E \text{ (mSv)} = D\text{x}0.7\text{x}0.2\text{x}365\text{x}24 \quad (2)$$

The yearly effective dose (mSv) in 2015 was from 0.014 to 0.087, while in 2016 it was from 0.006 to 0.081 and they are the same order of magnitude as values determined on other locations in our country [7]. Values of the strength of the absorbed dose of gamma radiation and yearly effective dose of external exposure to gamma radiation based on the content of natural radionuclides in the soil are in the range of expected values and are close to average values in the world [3].

Table 3 *Transfer factors for (TF) ^{137}Cs, ^{40}K, ^{226}Ra, ^{232}Th and ^{238}U in samples of soil and moss collected in 2015 and 2016 in NP Djerdap and discrimination factor (DF)*

Locality (moss)	**TRANSFER FACTOR (TF)**					**DF**
	^{137}Cs	**^{40}K**	**^{226}Ra**	**^{232}Th**	**^{238}U**	**^{137}Cs/^{40}K**
			2015			
1 (1)	1.06	1.06	1.18	0.26	0.28	1.00
2 (1)	0.30	0.38	1.39	0.70	0.21	0.78
3 (2)	0.54	1.16	0.83	0.28	0.30	0.47
4 (1)	0.81	0.44	0.87	4.49	0.03	1.86
(1)	2.45	0.36	0.95	0.57	0.10	6.84
5 (2)	1.12	0.24	0.73	0.83	0.15	4.75
(3)	1.48	0.32	0.97	0.29	0.17	4.64
			2016			
1 (2)	0.17	0.50	0.73	0.28	0.54	0.34
2 (2)	0.27	0.40	0.78	0.40	1.70	0.68
	1.03	0.28	0.17	0.16	0.60	3.68
3 (2)	0.26	0.47	0.57	0.24	0.69	0.55
4 (2)	0.92	0.54	0.44	0.34	0.36	1.70
5 (2)	1.99	3.38	3.83	3.68	8.60	0.59
(1)	0.21	0.06	0.79	0.31	0.96	3.50
6 (1)	0.39	0.55	0.23	0.41	0.54	0.71
(2)	0.51	0.64	0.52	0.70	1.11	0.80
7 (2)	0.10	1.37	1.29	1.41	4.84	0.07
(2)	1.00	0.87	1.40	0.69	1.44	1.15
8 (2)	0.59	0.84	0.69	0.54	1.86	0.70
(3)	0.99	0.65	0.86	1.30	1.35	1.52

The transfer factor (TF) is defined as the ratio between the content of a given radionuclide in a plant (Bq/kg) and the content of the given radionuclide in soil (Bq/kg) for dried plant and soil samples. Transfer of radionuclides from the soil to plants depends on physical, chemical and biological factors [8,9]. Table 3 shows that TF for ^{137}Cs is 0.10-2.67, ^{40}K 0.06-3.38, ^{226}Ra 0.1-3.83, ^{232}Th 0.16-4.49, ^{238}U 0.03-8.60. It is known that plants cannot differentiate between ^{40}K and ^{137}Cs in the take-over process as they have common chemical properties and belong to the same group in the Periodic system. It is general knowledge that ^{137}Cs enters the plant via its root and foliar deposition from the atmosphere. The discrimination factor (DF) defined as the ratio between the transfer factor of ^{137}Cs and transfer factor of ^{40}K enables determination of the radionuclides that is more easily absorbed into the plant. The values of DF are shown in table 3. Values of DF lower than 1 indicate that ^{40}K is more easily and efficiently absorbed than ^{137}Cs.

CONCLUSION

Radionuclides belonging to the radioactive series of uranium ^{238}U, ^{226}Ra and thorium (first member ^{232}Th), natural isotope ^{40}K, and also the artificially produced radionuclide ^{137}Cs were detected and measured in all investigated samples The average values of radionuclide content (Bq/kg) in soil collected in 2015 and 2016 were in the range of average values of radionuclide content in soil in the world, and in moss it was in the range of our previous research. The content of ^{137}Cs in soil and moss indicates that there was no new pollution with this radionuclide on the investigated territory. Determined values of the strength of the absorbed dose of gamma radiation and yearly effective dose originating from external exposure to gamma radiation based on the content of natural radionuclides in the soil were in the range of expected values and are close to average values in the world.

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THE COPEPOD DIVERSITY (Crustacea: Copepoda) OF SNR "OBEDSKA BARA"

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Abstract

The copepod presence is essential in all types of aquatic ecosystems. They have an important role in food chains as a necessary link between the producers, consumers and decomposers. The species diversity, abundance and seasonal population dynamics of copepods are parameters which could very accurate and sensitive assess the conditions of all aquatic ecosystems, freshwater or marine. Copepods could be used as the bioindicators for water quality, eutrophication, pollution levels and presence of contaminants. Variations in one or more of the numerous abiotic and biotic factors could lead to stress, migrations, death of copepod individuals and vanishing their entire populations in certain ecosystems. The water samples for qualitative and quantitative analysis of copepod status were taken using Standard Ruttner Water Samplers with plankton nets. During six months research period four genera: Acanthocyclops, Cyclops, Eucyclops and Eudiaptomus were detected at two localities at SNR "Obedska bara", with the dominant presence of C. vicinus and E. gracilis. According to the obtained results, the burning issue is the anthropogenic influence on copepod status in the SNR "Obedska bara", due to fluctuation in water levels, periodic drying out of the canals and inadequate and excessive pesticide application in surrounding area.

Keywords: Copepods, Zooplankton, Obedska bara, Species diversity, Bioindicators

INTRODUCTION

The copepods (Crustacea: Copepoda) are frequently found in almost all aquatic habitats, such as the water column and bottom sediments in lakes and oceans, subterranean waters and small surface water bodies – temporary ponds and puddles [1]. According to the same authors, three copepod orders dominate in fresh water bodies: calanoids, harpacticoids and cyclopoids. The calanoids are mainly herbivorous, the harpacticoids omnivorous, and the most of the cyclopoids are the strong predators. Although, many cyclopoid species could be commensals or parasites on certain hosts, such as fish, whales, molluscs, sponges and corals, larger species tend to be aggressive predators feeding on protozoans, rotifers, larvae of different insect species and small aquatic animals. Many cyclopoid species feed on algae, but the mixed diet, including the animal proteins, is necessary for the normal reproduction and egg forming [1]. Therefore, the copepods have an important role in maintenance and enrichment of food chains, as they represent a necessary link between the primary producers, consumers and decomposers in all aquatic ecosystems.

The Special Nature Reserve (SNR) „Obedska bara“ is a large swamp-forest area along the Sava river. It is the oldest protected area in Serbia, and one of the oldest natural resources in the world, as it was placed under protection in 1874. Since 1977 SNR „Obedska bara“ has proclaimed as a swamp area of the international significance by the Ramsar Convention, and included in the List of areas of special significance for the birds of Europe of Important Bird Area (IBA) project, and UNESCO's list of the world's most important wetland areas. Today, the SNR „Obedska bara“ represents the largest flooded area in Serbia, with authentic fragile wetland vegetation, wet meadows and forests, characterized by an exceptional biodiversity richness and significant presence of rare and endangered species of national and international importance. Therefore, the three-stage protection regime was established on a total area of 9,820 ha: I degree 315 ha, II degree 2,565 ha and III degree 6,940 ha. A protective zone of 19,611 ha was also established within the protection regime of SNR “Obedska bara”.

The copepods, as well as other aquatic organisms, prefer habitats which have stabile and constant physical, chemical and biological features. Although the SNR „Obedska bara“ is protected area, it is still exposed to fluctuations of the abiotic factors and strong anthropogenic influence. Variations in one or more of numerous abiotic, biotic and anthropogenic factors could lead to stress, migrations, death of copepod individuals and vanishing their entire populations in certain ecosystems. According to Balakrishna *et al*. [2] zooplankton has been widely used in aquatic pollution assessments, as they are sensitive to small changes in the environment. Therefore, the copepods are frequently used as the bioindicators for water quality, eutrophication, pollution levels and presence of contaminants. The aim of this study was to obtain the preliminary results on the copepod species diversity, abundance and seasonal population dynamics as parameteres which could sensitive and accurate assess the conditions of SNR „Obedska bara“.

MATERIALS AND METHODS

The study was conducted from June till December in 2017 at SNR “Obedska bara”, at two localities: “Obrež” and “Kula” (Figure 1). The water was sampled monthly using Standard Ruttner Water Samplers (1000 ml volume), from the boat, at the central position of the canal. To increase the positive sampling results the plankton nets were used. All samples were stored in plastic bottles, labelled and transported to the laboratory for the further analysis. The copepods were identified according to standard determination keys, particularly based on the adult’s morphological characters.

RESULTS AND DISCUSSION

During six months research period five copepod species from two order were collected: *Cyclops vicinus* Ulyanin, 1875, *Acanthocyclops robustus* (Sars G.O., 1863), *Acanthocyclops vernalis* (Fischer, 1853), *Eucyclops serrulatu*s (Fischer, 1851) and *Eudiaptomus gracilis* (Sars G.O., 1863).

The most abundant were *C. vicinus* from the order Cyclopoida and *E. gracilis* from the order Calanoida (Table 1). The highest abundance of all five species at both prospected localities was detected in November. The low number or absence of the observed copepod species during the summer and winter months could be explained by the direct influence of temperature as the main abiotic factor that induce the dormancy or diapause. According to Marten and Reid [1], the capacity of copepods to induce the dormancy or diapause helps them to survive in shallow and small water bodies that drastically change the water level or even dry periodically, such as the case with SNR “Obedska bara”. The dormancy could range from simple latency in which copepods usually respond to an immediate and fast stimulus, such as the temporary drying, to the true diapause in which they react to the environmental changes.

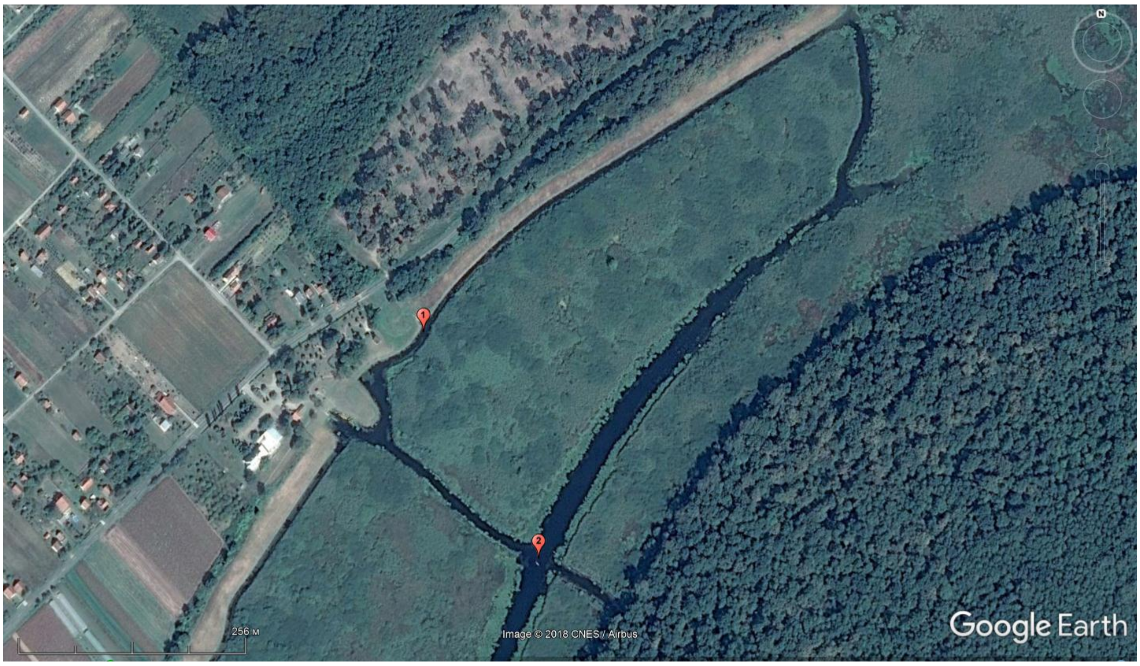

Figure 1 *The sampling localities at SNR „Obedska bara" (red dots)*

Table 1 *The adult copepod abundance found at SNR „Obedska bara" (ind/1000ml)*

Month	*C. vicinus*		*A. robustus*		*A. vernalis*		*E. serrulatus*		*E. gracilis*	
	Obrež	Kula	Obrež	Kula	Obrež	Kula	Obrež	Kula	Obrež	Kula
June	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
July	0.00	0.00	0.67	0.00	0.67	0.00	2.00	0.00	1.33	0.00
August	0.00	0.67	0.00	0.00	0.00	0.67	0.00	0.67	0.00	0.00
September	2.00	2.00	0.00	1.33	0.00	0.67	0.00	1.33	0.00	2.00
October	1.33	2.00	1.33	0.67	2.00	1.33	2.00	1.33	1.33	1.33
November	**4.00**	1.33	**3.33**	2.00	0.67	**3.33**	1.33	**3.33**	2.67	**4.00**
December	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Average	1.05	0.86	0.76	0.57	0.48	0.86	0.76	0.95	0.76	1.05

The true diapause is frequent and wide spread among freshwater cyclopoids. It induces the slowing of metabolism and the development interrupting for a long period of time and usually occurs in certain developmental stages. The abiotic and biotic factors that could provoke the diapause are: photoperiod, temperature, poor or no food sources, or the combination of these factors. The diapaused copepods can survive for a long period of time in the sediment of the temporary water bodies with no free water present, as long as the water content in sediment exceed 15% [1]. There are several explanations for the copepods diapause initiation or termination, such as: temperature, photoperiod, density, predator kairomones, food quality, maternal necessity. According to Seebens *et al*. [3], high predation pressure during summer and the dependency of herbivorous nauplii on a high food availability, could also be the ultimate cause for the summer diapause of *C. vicinus*.

The copepods are also distinguished by their vertical migrations, which could be ontogenetic, seasonal or diel. The ontogenetic migrations are caused by the metamorphosis of certain life stages. The copepods reproduce sexually and have a complex life cycle of six naupliar stages, five copepodid stages and an adult stage. Depending on the species, temperature, and food supply the life cycle can mature from an egg to an adult in a few days or weeks. The diapause in copepods life cycle could occur through the egg production or due to an interruption of the development, usually within an advanced copepodid stage [3]. The seasonal migrations are determined by the water regime and period of the year, especially by the seasonal changes of water temperatures, saturated oxygen, pH, available food sources and predation. SNR "Obedska Bara" has specific hydrological features and frequent water deficit, where the reduction of open water surfaces and weak flow, especially during the summer and winter months, are mainly caused by the human interference. Low population densities and species diversity of copepods could be also conditioned by their annual fluctuations. Normally, zooplankton abundance is higher in spring and autumn and lower in summer and winter, as their abundance is limited by nutrient availability [4]. According to Ratajac [5], in shallow lakes copepods are susceptible to dial vertical migrations, migrating from the water surface to the bottom depending on numerous factors. The abundance and the food quality were important determinants of *C. vicinus* densities, as the first and the most abundant generation developed during the spring algal bloom [6].

The low number of copepod collected specimens and species at SNR "Obedska bara", especially during prospected months, could be explained by the pesticide contamination. Although, this area is protected by the national and international laws, it is still under strong influence of anthropogenic factors, as it is surrounded by numerous agricultural fields and orchards. Zooplankton are one of the most sensitive animal groups to the toxic effects of the chemicals [7]. Regarding the copepods, pesticides almost always lead to their elimination in freshwater biocoenoses. Day [8] stated that zooplankton accumulate persistent lipophilic chemicals, particularly the organochlorine pesticides to concentrations greater than in the environment, and therefore contribute the pesticide residues maintenance and increase in the higher trophic levels. Although Hansen and Jeppensen [6] emphasized that cyclopoid copepods are well adapted to their environment if herbivorous stages coincide with peak availability of food and coordinate their life cycle in manner to avoid competition and predation, they could not compete with high agrochemical contamination.

The organophosphate insecticides, synthetic pyrethroids, many herbicides and their residues may not be detectable in the organisms (they will not be bioaccumulated to any level) and may not have no observable biological effects, but still, some organisms, such as copepods, may experience a toxic effect [8]. Therefore, chemicals and their residues present a problem in the assessment of the environmental damage, especially from pesticide contamination.

CONCLUSION

During six months research, period five copepod species from two order were collected: *Cyclops vicinus* Ulyanin, 1875, *Acanthocyclops robustus* (Sars G.O., 1863), *Acanthocyclops vernalis* (Fischer, 1853), *Eucyclops serrulatus* (Fischer, 1851) and *Eudiaptomus gracilis* (Sars G.O., 1863). The most abundant were *C. vicinus* from the order Cyclopoida and *E. gracilis* from the order Calanoida. The species diversity and abundance of copepod species are correlated with the numerous abiotic and biotic factors. According to the obtained results, the main factors that influence the copepod species diversity at SNR "Obedska bara", their abundance and seasonal dynamics are seasonal water level changes and the anthropogenic influence, especially the inadequate and excessive pesticide application in surrounding area. The human irresponsible behaviour and negligence could have devastating effects on the biodiversity of protected areas, such as SNR "Obedska bara". Therefore, the area of I and II degree protection should be extended and continuously monitored.

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OVERVIEW OF HARMONIZATION OF WATER MONITORING LEGISLATION IN SERBIA WITH WFD REQUIREMENTS: CASE STUDY IN NOVI SAD

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Abstract

In the past years, water monitoring practice in Serbia, based on the Law on Water, was mainly focused on physico-chemical parameters and analysis only of inorganic compounds. After becoming candidate country Serbia had the obligation to adapt existing, or develop new legal documents to be able to implement EU legislation in all fields, including water quality monitoring. However, it is still not fully applied, due to the equipment limitations and lack of expertise. Water Framework Directive, in Article 16, defines strategies to prevent and minimize water pollution with the aim to achieve the 'good' status of all water bodies within the member states. For a water body to be in overall 'good' status both ecological and chemical status must achieve minimum a 'good' status. Serbia is still a long way from achieving the 'good' status on the majority of its water bodies, and one of the main reasons is that, currently it is impossible to obtain quality analytical results. The aim of this paper was to apply monitoring and risk assessment procedures defined in the WFD, on wastewater and Danube surface water in the city of Novi Sad. Furthermore, the objectives of study were to check the compliance of water monitoring legislation in Serbia with requirements of WFD and to identify the gaps in the procedures and legislation in order to demonstrate the results to the relevant institutions in Serbia in charge of conducting obligatory monitoring.

Keywords: Water monitoring, Water framework directive, Prioritization, Risk assessment

INTRODUCTION

Serbia regulates the water quality monitoring procedures within the Law on Water (Official Gazette of Republic of Serbia, No. 30/10, 93/2012 and 101/2016). In the past years monitoring was mainly focused on the physico-chemical parameters and analysis of inorganic compounds, while organics were entirely neglected. After becoming candidate country in 2012, Serbia had to harmonize all existing regulation and develop new legal documents to implement the EU legislation in all fields, including water quality monitoring. Part of the legislation has already been harmonized, but it has not been fully implemented. For instance, the Serbian Regulation on emission limit values of priority and priority hazardous substances which pollute surface waters and deadlines for their achievement (Official Gazette of the RS, No. 24/2014), which is in accordance with the EU legislation has been adopted in 2014, but it is still not fully applied, due to the equipment limitations and lack of expertise.

In the European Union, the Article 16 of Water Framework Directive (WFD), defines strategies against water pollution with the aim to achieve the good status of all water bodies within the member states. For a water body to be in overall 'good' status, both ecological and chemical status has to be no less than the 'good' grade. The chemical status can be considered as good if 33 priority substances and priority hazardous substances, defined in Directive on

Environmental Quality Standards (EQS) 2008/105/EC (also known as Priority Substances Directive), which are regulated and monitored at the EU level, comply with the legally binding environmental quality standards. Directive 2013/39/EU adopted in 2013 as an amendment of the Directives 2000/60/EC and 2008/105/EC brings additional EQS for 12 new substances, adds EQS in biota for 8 substances and updates some surface water EQS. The Article 8 of the WFD sets out the monitoring requirements in the member states, while The Annex V defines three monitoring types: surveillance, operational and investigative monitoring. The priority list substances discharged into the river basin or sub-basins must be monitored, while other pollutants also need to be monitored, if they are discharged in significant quantities in the river basin or sub-basin.

Monitoring of the quality of surface water in Serbia is conducted by the Serbian Environmental Protection Agency (SEPA) in accordance with the Article 109 of the Law on Water (Official Gazette of Republic of Serbia, No. 30/10, 93/2012 and 101/2016). Reports on the monitoring of the quality of surface and groundwater are published annually and contain following information: (1) results of examination of biological elements for evaluation of ecological status of surface water, (2) results of analysis of physico-chemical, chemical and microbiological parameters in surface water and groundwater, and (3) results of examination of the quality of sediment in rivers and accumulations. Parameters are selected based on the Regulation of parameters of ecological and chemical status of surface water and parameters of chemical and quantitative status of water (Official Gazette of RS, No. 74/11), Bylaw on definition of annual monitoring programme of status of water for 2015 (Official Gazette of RS, No. 46/15), Regulation on emission limit values of priority and priority hazardous substances which pollute surface waters and deadlines for their achievement (Official Gazette of the RS, No. 24/2014), Regulation on emission limit values of polluting substances in surface and groundwaters and deadlines for their achievement (Official Gazette of the RS, No. 50/2012) and the requirements set in the WFD. The SEPA Report for 2016 [1] included analytical results for majority of priority and priority hazardous substances from 45 water bodies in Serbia. However, due to the limitations of the equipment and lack of expertise, presented analytical results in most of the cases were below LOD and LOQ.

Additional monitoring of surface water for organic compounds in Serbia has been conducted through several international projects in the past years. The NATO Science for Peace Project - ESP.EAP.SFPP 984087 included monitoring of wastewater, surface water and raw water used for production of drinking water in the city of Novi Sad(Serbia) from 2012-2013. The obtained results from target [2] and non-target [3] analyses pointed out on presence of various organic compounds in the aquatic matrix. The 3rdJoint Danube Survey in 2013 [4], monitored the quality of Danube on 20 sampling locations in Serbia, including two locations upstream and downstream of the city of Novi Sad. As the application of the non-target screening analysis is neither regular nor obligatory, the specific information about the occurring priority and priority hazardous compounds is nonexistent or, in the best case scenario, scarce. Even though through non-target screening data on various occurring compounds can be obtained, it does not reveal information about the risk of these compounds to living organisms in surface water and consequently to human health. To perform a quality risk assessment for detected substances, good practice is indicating that screening analysis should be followed by target analyses for specific location, to obtain concentration levels used in calculation of possible risk. The risk assessment is of considerable importance, especially for the sensitive locations, as the city of Novi Sad, since the surface water filtrated trough natural bank-filtration process is used as raw water for production of drinking water.For the purpose of conducting the risk assessment and obtain the risk index for detected priority and hazardous priority substances,the prioritization procedure has to be applied for all water bodies in order to define the specific, most relevant pollutants present in the research area.

The prioritization techniques have evolved in the last 20 years, and since the adoption of the WFD it has become the obligatory procedure in the EU member states. The Combined Monitoring based and Modeling-based Priority Setting (COMMPS) procedure was the first European wide prioritization exercise that resulted in the current list of priority settings (PS)[5]. In that study, emphasis was given to the availability of complete exposure and hazard information, reducing the list of evaluated substances to only 279, disregarding potentially problematic substances with limited data sets. The analytical techniques and the limits of quantification available at that time, further limited the number of possible detections [5]. A similar approach was applied in the prioritization study carried out for the revision of the first list of PS. According to the Article 16 of the WFD, the list of PS needs to be reviewed every four years. The revision of the first list of PS (which is still under way at the time of writing) involved two distinct prioritization procedures: a monitoring-based prioritization study conducted by L'Institut National de l'EnviRonnementIndustrielet des RiSques (INERIS), hereafter referred to as "INERIS study", and a modeling-based prioritization study conducted by Joint Research Center (JRC) [6]. The monitoring-based study, which is the one most frequently referred to in this article, assessed a larger number of substances (339) compared to the COMMPS study and could rely on a more extensive database of environmental observations and a refined hazard assessment, which is discussed more closely in the "Materials and methods" section. The modeling-based prioritization exercise again evaluated a total of 2034 compounds according to pre-defined hazard and exposure criteria that yielded 78 substances of potential high concern, for which a more intensive assessment was performed [6]. The modeling-based approach used a risk scoring that ranged from 1 to 5, which therefore did not allow for a quantitative assessment based on PEC/PNEC ratios, where PEC stands for Predicted Environmental Concentration, and PNEC for Predicted No-Effect Concentration.

Monitoring and risk assessment procedures defined in the WFD, were applied on the results of wastewater and Danube surface water analysis, in the city of Novi Sad, with the aim to show a good practice for monitoring of organic pollutants in water, particularly priority and hazardous priority substances. The good practice is demonstrated as the algorithm of over-all process of identification, detection, quantification, prioritization and finally calculation of risk index, which gives real and relevant data for specific location, and identifies the missing steps in the procedures and legislation, and possible stages that should be considered for implementation in obligatory monitoring.

MATERIALS AND METHODS

Selection of sampling locations

Based on the location of the entire sewerage network in the city of Novi Sad, 9 sampling points have been selected for the campaigns. Four sites were located within municipal wastewater collectors (GC1', GC2', RO', RP'), and five were in the Danube's riverbed (RI, GC1", GC2", RO", RP"). Information and location of the sampling sites are given in Figure 1. The sampling site RI was located upstream of the city of Novi Sad, before all discharge points, and it has been selected in order to assess the eco-toxicological status of the river Danube prior to any local urban impact. Analysis of wastewater from the sewerage system determined the level of contamination of municipal and industrial wastewater streams, which are discharged directly into Danube without any treatment. Danube surface water has been sampled 100 m downstream of each discharge in order to assess the impact of wastewater streams on eco-toxicological status of the river. The sewage system at the sampling site RO' was located in the area of the water supply source and downstream close to the industrial part of the city with the Oil Refinery, thermoelectric and heat generating plant. The RP' was located on the other bank of the river in agricultural area and in the vicinity of plant for production of diagnostic reagents, laboratory chemicals and solvents. The sampling sites GC1" and GC2" were located on the stretch near or under three bridges indicating the water runoff from the bridges as possible source of Danube surface water pollution.

Figure 1 *Location of sampling sites within the city of Novi Sad*

The screening and target analysis methods

The screening and target analyses methods and procedures have been explained in detail by Miloradov *et al.* [2] and Milić *et al*. [3]. For the screening analyses liquid-liquid extraction coupled with the GC-MS system was used. For the purpose of the target analyses the procedures used for quantitative analyses of selected compounds were: for the WFD pollutants - ISO 6468 (WFD pollutants),ISO 10301(VOCs), DIN EN 17025(tributyltin compounds),modified ISO 11369 (simazine, atrazine, isoproturon, diuronand hormones).

The ecotoxicity assessment

From the scope of several thousands of identified substances during the screening analyses, approximately 300 compounds from diverse chemical groups have been selected for target analyses and further ecotoxicity (risk) assessment. Quantitative Structure-Activity Relationships (QSAR) approach was used to predict toxicity of selected identified organic pollutants based on their chemical structure. As the results of this analysis, lowest values of Predicted No Effect Concentration (PNEC) were obtained for 350 compounds. The PNEC values in this research have been obtained in three different ways: EU directives, ecotoxicity databases and QSAR approach based on the acute toxicity to the standard test organisms *Daphnia magna*, *Pimephales promelas*, as well as *Selenastrum capricornutum*.

The prioritization process – applied approach

Applied prioritization approach is based on the evaluation of the exceedance of environmental threshold values - PNEC, for all organic compounds monitored in the wastewater, Danube water, and raw water used for production of drinking water [7,8]. In order to identify the extent of exceedance of eco-toxicity thresholds, the PNEC value for each analyte was compared to the Maximum concentration (MC), obtained within TA. The MC/PNEC ratio is the indicator for ranking of all compounds of concern according to their relevance and potential negative impact on living organisms in aquatic environment. Only compounds with MC/PNEC ratio above 1 were marked as relevant and presented in this paper.

RESULTS AND DISCUSSION

The results of the Novi Sad case study have been summarized into the algorithm that shows good practice of PHPs monitoring plan for location of high risk wastewater pollution of natural recipient and raw water source (River Danube), as it is locality of Novi Sad. The shown procedure should be followed for every location, even if for low risk locations, but the frequency of every module (stage) of algorithm should be modified and optimized to fit the specific locations needs and requirements. The algorithm of goodregular surveillance monitoring practice is presented in Figure 2.

Results of calculated prioritization based on the comparison of maximum concentration levels obtained within TA and eco-toxicity thresholds are presented in Table 1. Pollutants are ranked according to their relevance and threat to human population and the environment. Priority list in Table 1 should be the focus of the monitoring in the future, beside the WFD priority substances, since it represents the highest risk to the health of the humans. The most hazardous compounds are linear and branched alkanes, which can be explained by proximity of the Oil refinery. Other important groups of compounds include hormones, pesticides, industrial chemicals, and PAHs.

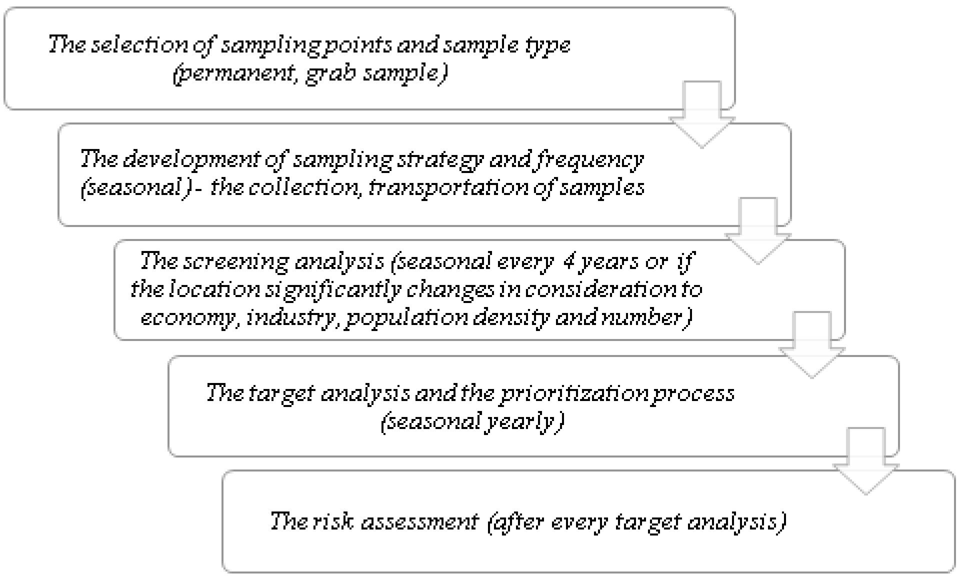

***Figure 2** Algorithm of good practice for surveillance monitoring of PHPs*

Table 1 *Results of MC/PNEC ratio*

Compound/NIST lib.	PNEC [ng/L]	Max. conc.	MC/PNEC
Heptachlor	0.0002	420	2100000.0
Heptachlor epoxide	0.0002	50	250000.0
Benz(a)anthracene	1.8	210	116.7
Fluoranthene	6.3	510	81.0
DDT-4,4'	10	500	50.0
Endosulfan-alpha	5	230	46.0
Chlorpyrifos	1	40	40.0
Dieldrin	10	270	27.0
DDD-4,4'	25	620	24.8
Pyrene	20	490	24.5
Phenanthrene	30	360	12.0
PCB-194	0.2	1.2	6.0
Hexachlorocyclohexane-gamma	5.5	30	5.5
Octylphenol	100	540	5.4
Hexachlorobenzene	10	50	5.0

Compound/NIST lib.	PNEC [ng/L]	Max. conc.	MC/PNEC
DDE-4,4'	25	110	4.4
Trichloromethane	2500	9720	3.9
Nonylphenol	300	1150	3.8
4-nonylphenol	300	1140	3.8
1,2-benzenedicarboxylic acid. dibutyl ester	600	2150	3.6
Anthracene	100	280	2.8
Di(2-ethylhexyl)phthalate (DEHP)	1300	2630	2.0
Fluorene	100	140	1.4
Chrysene	100	130	1.3
4-(1,1,3,3-tetramethylbutyl)-phenol	100	110	1.1
Toluene	4300	4410	1.0
Trifluralin	30	30	1.0

CONCLUSION

Comparing the SEPA Report and conducted procedure, which is in accordance with the WFD requirements, it is obvious that the main issue in Serbia is the lack of the quality of analytical results. Even though, legislation is significantly harmonized, it cannot be fully implemented due to incompatible and outdated equipment and the lack of expertise of the staff in charge. For this reason, the majority of the obtained analytical results on organic compounds isbelow the LOQ and LOD, and therefore unquantified, which is not sufficient input for valid ecotoxicity and prioritization procedure. The results of the Novi Sad case study have been summarized into the algorithm that shows good practice of PHPs monitoring plan for location of high risk wastewater pollution of natural recipient and raw water source (River Danube), as it is locality of Novi Sad. The shown procedure should be followed for every location, even if for low risk locations, but the frequency of every module (stage) of algorithm should be modifies and optimized to fit the specific locations needs and requirements. The only solution to this is investing significant funds in providing modern, up-to-date instruments and high-quality training for the staff of the Agency in charge of conducting environmental analysis in Serbia.

ACKNOWLEDGEMENT

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THE IMPACT OF STORAGE OF EXPLOSIVES IN THE UNDERGROUND WAREHOUSE "MUŠIĆI" RMU "BANOVIĆI" ON THE QUALITY OF MINE AND ATMOSPHERIC AIR

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Abstract

The exploitation of coal in the RMU Banovići is done with a classic discontinuous exploitation system which, among other things, includes mining operations with the use of various explosive devices. In order to achieve the planned goals, explosive devices are stored in an underground warehouse that is well-ventilated. The location of the warehouse is in the immediate vicinity of residential buildings and regional road R 471 which connects Banovići and Lukavac. Due to the way of ventilation of the warehouse and the fact that explosive devices of sensitive chemical composition are stored in the warehouse, this study will show the effects of storage of explosives on the mining air in warehouse, as well as the impact of the spent air current on the quality of atmospheric air in the immediate vicinity of the warehouse.

Keywords: Explosive, Warehouse, Storage, Air quality

INTRODUCTION

The production processes for obtaining coal in the RMU Banovići are carried out in two production plants, the Coal Exploitation Coal Mine and the Underground Exploitation Mine. In both plants, drilling mining works are used as the first working procedures. Explosives are used for mining. In order to ensure the reliability of the realization of the planned goals, it is necessary to store a certain amount of explosive devices.

In the case of manipulation with explosive devices, the legal regulations governing this field must be observed not only for reasons of stability of miner technical characteristics of explosive substances, but also for the purpose of neutralizing the harmful effect of these chemical compounds on atmospheric and mine air.

This paper will analyze the listed harmful effects documented for many years by performing measurements of the mining air in the interior of the warehouse as well as the atmospheric air in the immediate vicinity of the outgoing air current with which the warehouse is ventilated.

Position and description of warehouse explosive means of Mušići

The warehouse of explosives Mušići is located at the entrance to the town of Banovići near the former factory Borac ready-made clothes Travnik and Renix building materials warehouses. It is about 150m away from the regional road BanovićiLukavac R-471.

The werehouse was built as an underground storage in serpentine material. It consists of an entrance hallway, access corridors, a chamber for the accommodation of explosives and initials, ventilation ducts and countermeasures (Figure 1). The premises of the warehouse are covered with bricks and dismantled with cement mortar, and under the warehouse it is made of concrete slabs [1].

The ventilation of the warehouse is depressed under the influence of mechanical energy generated by an axial fan of 7.5 kW power. The inlet air into the storage rooms is introduced through the venthole above the chamber for the accommodation of the initial means (Figure 1, detail 1) and entry into the warehouse (Figure 1, detail 2). The outgoing air current is output from the storage through the installed fan (Figure 1, detail 3).

The ventilation of the warehouse is done according to the prescribed regime. The fan fires about half an hour from the time when workers need to enter the warehouse to issue or receive explosive devices. If necessary, the fan may light up and shrink when it is necessary to keep the humidity value within the allowed limits. For the ventilation of the warehouse, the required air volume is about 252 m^3/min, and for explosion chambers individually 84 m^3/min [1].

Explosive and explosive materials which are in warehouse

The underground warehouse "Mušići" belongs to the category of underground mining facilities. The warehouse was built in 1958. It is designed to store commercial explosives.[2] Commercial explosives that are stored are:

- AN-FO explosives. The basic component of these explosives is ammonium nitrate (NH_4NO_3) about 94-95% and diesel fuel (CH_2) 5-6% [3].
- Nitroglycerin plastic explosives. These explosives contain more than 80% nitroglicerol ($C_3H_5N_3O_9$) nitroglycol C_2H_2 $(ONO_2)_2$ nitrocellulose in gelatinous state, as well as other organic and inorganic components in a small percentage [3].

In the warehouse Mušići, also initial tools are stored electric and non-electric detonators, busters detonating and slow-burning cords.

In order to preserve their chemical stability, explosive substances must be stored in accordance with the manufacturer's instructions.

Permitted quantities of explosives that can be stored in a warehouse are given in the following table.

Table 1 *Permitted quantities of explosives and initial substances that may be stored in chambers*

Number of chamber	Explosive materials	Quantity
1.	The initial funds Retardants	114 000 kom 12 000 kom
2.	Powder explosives	16 512 kg
3.	Plastic explosive	17 738 kg
	Slow-burning cords Detonating cords	10 000 m 100 000 m
4.	Powder explosives Powdery methane explosive	8 263 kg 7 791 kg

Control of quality of mining air

Due to the storage of explosives in changing conditions (temperature, humidity), there may be vapors that may adversely affect the work comfort and health of workers. In order to neutralize negative impacts, the analysis of air quality in the premises of the warehouse is carried out (mine air). Analysis of mining air includes the following controls:

- ✓ Oxygen (O_2)
- ✓ Carbon dioxide (CO_2)
- ✓ Carbon monoxide (CO)
- ✓ Metan (CH_4)

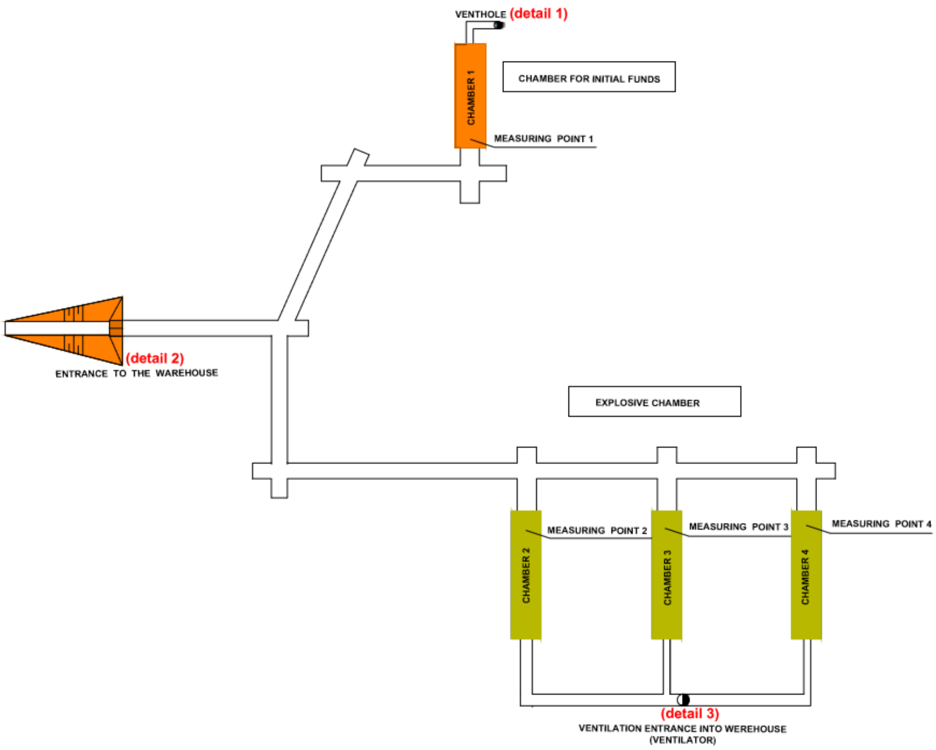

Figure 1 *Sheme warehouse of explosives Mušići with measuring points*

The air samples are taken at four places in each chamber (Figure 1). Sampling is done with a rubber ball for taking samples of air for chemical analysis [4]. Samples taken are analyzed in the laboratory. Measurements are done 2 times during the month, and if necessary and extraordinary. The values of the concentrations of the controlled components must not exceed the maximum permissible concentration (Table 3). Sampling is done at a time when the ventilation is not working.

Table 2 *Report on the quality of the air in the warehouse explosives*

Place of sampling	Date	Concentration			
		CO_2(%)	CH_4(%)	CO(ppm)	O_2(%)
chamber I	13.1.2016	0.03	0.04	0.95	20.61
chamber II		0.03	0.01	1.53	20.62
chamber III		0.02	0.01	1.40	20.60
chamber IV		0.04	0.00	1.04	20.61

Table 3 *Maximum permissible concentrations in mining air*

CO_2 (%)	CH_4 (%)	CO (ppm)	O_2 (%)
to 1 %	to 1.5 %	to 5	min 19 %

Quality control of atmospheric air in directly nearly warehouse explosive means

In the process of decomposition of explosive substances, harmful gases occur as a side effect. The most common are nitrosal gases that are dispersed in the surrounding atmosphere.

Also, in the processes of production, storage and manipulation, certain concentrations of harmful substances in the air are distinguished. In this connection, it is necessary to regularly check the effect of the air current, by measuring the emission of harmful substances that are separated from the mining air in atmospheric air.

As a result of ventilation using a ventilator with depression mode, the largest concentrations of volatile particles are at the measuring point MM1 (Figure 2). This site is treated as a source of pollution. For the purpose of controlling the impact on the wider environment, measurements are carried out in the immediate vicinity of the warehouse at a distance of up to 150 meters at the measuring points MM2 and MM3 (Figure 2). During sampling ventilation must work.

Figure 2 *Position of the warehouse of explosives Mušići with measuring points*

Measurement results

***Table 4** Tabular display of measurement results*

Measurement place 1 -Ventilation entrance into warehouse of explosives "Mušići" (ventilator) (MM1)				
TYPE OF MEASUREMENTS	I measuring	II measuring	III measuring	IV measuring
NO_2 (mg/m^3)	**0.012**	**0.010**	**0.007**	**0.008**
Wind speed (m/s)	0.5	0.8	0.12-1.2	0.0
Wind direction	northwest	north	northeast	no wind
Air temperature (°C)	18	19	7.6	-3
Relative humidity (%)	78	76	86	84
Atmospheric pressure (hPa)	982	984	962	962
Measurement place 2 - Warehouse of building material (MM2)				
NO_2 (mg/m^3)	**0.001**	**0.000**	**0.001**	**0.001**
Wind speed (m/s)	0.4	0.3	0.12-1.2	0.0
Wind direction	northwest	north	northeast	no wind
Air temperature (°C)	18	19	7.6	-3
Relative humidity (%)	76	75	86	84
Atmospheric pressure (hPa)	983	985	962	962
Measurement place 3 - Residential buildings north of the warehouse (MM3)				
NO_2 (mg/m^3)	**0.000**	**0.000**	**0.001**	**0.002**
Wind speed (m/s)	0.6	0.8	0.12-1.2	0.0
Wind direction	northwest	north	northeast	no wind
Air temperature (°C)	18	19	7.6	-3
Relative humidity (%)	77	76	86	84
Atmospheric pressure (hPa)	982	984	962	962

***Table 5** Emission limit values NO_2*

Influence	Emission limit values NO_2 (μg NO_2/m^3)
Eco system	30
Health of workers	60

CONCLUSION

As presented in the previous exposition, the storage of commercial explosives in an underground storage does not cause the composition of the mine air that could endanger the conditions for normal operation, nor cause the health consequences of the workers (Tables 2 and 3).

Also, the spent air current (mine air) contains concentrations of harmful substances in quantity that does not endanger the quality of atmospheric air (Tables 4 and 5).

In accordance with the above, it can be concluded that the artificial ventilation of the warehouse is well dimensioned. It can also be concluded that explosives are properly stored in quantity and quality. What is necessary to emphasize is that ventilation is done according to the prescribed regime. Based on the results of measurements of atmospheric and mine air concentrations, it can be concluded that the ventilation regime is well established.

The author's recommendation is to strictly observe the prescribed capacity of the warehouse and to maintain the applied ventilation regime in the warehouse. In the case of storage of new types of explosives, monitor the mine and atmospheric air and, if necessary, change (reduce) the capacity of the warehouse and the ventilation mode.

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MODELLING SPATIAL DISTRIBUTIONS OF AIR POLLUTION CAUSED BY CHEMICAL ACCIDENTS

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Abstract

Chemical disasters are usually connected with supplying or transport systems of hazardous substances and they can cause heavy atmospheric pollution. It is necessary to predict the manner of pollutants spread, their concentrations, velocity and spread directions with the aim of accurate time warning or possible evacuation of the population. This paper analyzes and compares theory and application of chosen Gaussian dispersion model and software model ALOHA for the case of hazardous substances release. The results obtained by applying the models are important for the risk assessment conclusions.

Keywords: Air pollution, Chemical accidents, Dispersion models, Hazardous substances, Risk assessment

INTRODUCTION

The emission of hazardous gases into the atmosphere, either unintentionally due to human negligence, faults in plants, natural disasters, and transportation of dangerous goods or intentionally in terrorist attacks, represent a great danger to the population and infrastructure.Measurement is of great importance for determining the impact of concentration of hazardous gases on the population healthand the environment.Various physical and chemicalmethods can be used to measure concentration of hazardous gases. The measurements can be continuous (over a longer period of time) or discontinuous(measuring the concentration of gases in a shorter time interval), and the results can be presented in the form of a weight ratio of the dangerous substance and a gas volume unit, e.g. $\mu g/m^3$ or as a flow (mass of the dangerous component per the unit of time: mg/h, g/h and the like). The limit values for concentration of hazardous gases in the place of the accident are determined by regulations [1,2].

Modeling and simulation of the air pollution dispersion process are mathematical tools of great importance for the prevention or possible remediation of the consequences of pollution. To estimate the movement and dispersion of pollutants after their release into the atmosphere, numerous dispersion models have been developed. Physical models simulate a real phenomenon in laboratory conditions. They enable the definition of the dispersion mechanism and provide validation of data obtained from mathematical models.

Mathematical models of atmospheric dispersion, which describe the movement of pollutants in the air under the influence of wind (transmission) and turbulent atmospheric movement (diffusion) can be divided into deterministic and statistical models.Deterministic models are based on the fundamental mathematical description of the atmospheric processes and all cause-effect relations that affect the dispersion process. Statistical models are based on semi-empirical statistical relations derived from existing data and measurements.

The development of information technology enabled the rapid development of various dispersion models. They are becoming more and more complex and allow the use of a large number of input parameters. A large number of these systems are available on the market [3].

MATHEMATICAL MODELS OF POLLUTANTS DISPERSION

The atmosphere is a very complex physical-chemical system, so the modeling of this system is extremely complex. Atmospheric transport and dispersion of air pollutants depend on the movement of atmospheric masses (winds), the mixing of air masses by height, chemical reactions or radioactive decay in the atmosphere or the rate of precipitation/alluvion of pollutants [4].

Starting from the method of mathematical description of the process of dispersing the substance, three classes of the model for the analysis of air pollution can be distinguished: Lagrange, Euler and Gauss. Lagrange and Euler methods belong to the class of deterministic models by which the concentrations of dangerous gases can be calculated by different methods of solving the equation of turbulent diffusion.Most software applications for assessing air pollution dispersion, which are now used in practice, are based on the application of the Gaussian method, which belongs to the class of statistical models. Therefore, only the Gaussian model is presented in the paper.

Gaussian model

The statistical Gaussian model for the calculation ofground pollution concentration is the simplest model in terms of both the formulation and the number of necessary parameters. This made it the most widely used model in software packages which are used in drafting normative documents on air quality.

The basis of this model is the assumption that the impurities emitted by continuous point source form the plume in which the symmetric distribution of particle concentration is observed in relation to the axis of the plume, which is shown in Figure 1. The basic equation of the statistical Gaussian model is composed of two functions of the probability density of the normal distribution law and has the form [5,6]:

$$C(x,y,z) = \frac{Q\, f_F\, f_W}{2\pi\,\sigma_y(x)\sigma_z(x)} \exp\left(-\frac{y^2}{2\sigma_z^2(x)}\right)\left\{\exp\left[-\frac{(z-h)^2}{2\sigma_z^2(x)}\right] + \exp\left[-\frac{(z+h)^2}{2\sigma_z^2(x)}\right]\right\} \qquad (1)$$

where Q – is source emission rate; C – concentration of emission at any receptor location; $\sigma_y(x), \sigma_z(x)$ – dispersion coefficientsdefined either by stability classes or the time of movement from the source, where it is assumed that the direction of axes $0X$ matches the direction of the wind vector; $\bar{u}$ –mean wind speed at the level of measurement; h – effective source hight; f_F i f_W– corrections of the cloud of impurities due to the dry precipitation of impurities.

In the equation (1), σ_y and σ_z arehorizontal i vertical standard deviation of emission distribution. For determining these dispersions, the following relations are used:

$$\sigma_y = A\,x^a; \quad \sigma_z = B\,x^b \tag{2}$$

where A, a, B, b are coefficients which depend on the atmosphere stability and surface relief. These parameters for dispersion calculation are given in Table 1.

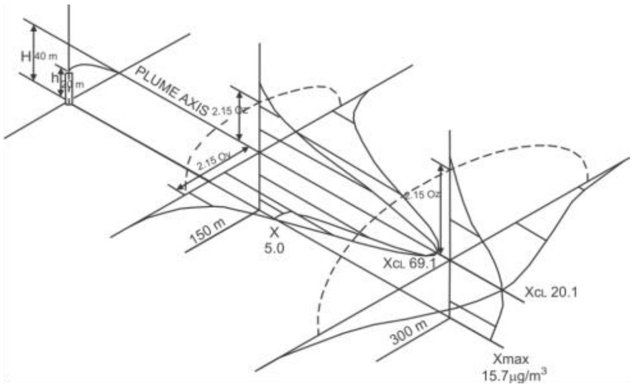


Figure 1 *Gaussian description of the emission of pollutants from a point source [5]*

Table 1 *Parameters for dispersion calculation [5]*

		A	a	B	b
Very unstable	A	0,527	0,865	0,28	0,90
Unstable	B	0,371	0,866	0,23	0,85
Slightly unstable	C	0,209	0,897	0,22	0,80
Neutral	D	A	a	B	b
Stable	E	0,128	0,905	0,20	0,76
Very stable	F	0,098	0,902	0,15	0,73

SOFTWARE FOR MODELING EMISSIONS OF DANGEROUS GASES

ALOHA (Areal Locations of Hazardous Atmospheres) software is a tool for estimating the movement and dispersion of gases in the direction of wind [7]. This air model estimates concentrations of pollutants downwind from the pollution sourcetaking into consideration physico-chemical characteristics of the pollutants, meteorological conditions at the time of the accidentand the circumstances under which the uncontrolled emission of the substance occurred.

The program’s keyfeatures are:

- The program gives a variety of scenario-specific output, including threat zone images and source strength graphs.

- Calculates the release rate change of chemicals from the tank or gas pipelines over time.

- Program models different release scenarios (toxic gas cloud, jet fires) and evaluates different types of hazard: flammability, overpressure, toxicity.

- Minimizes incorrect data entry by cross-checking the input values and warns of an impossible physical value.

- Contains its own chemical library with physical properties for about 3000 common hazardous chemicals so the user does not have to enter this data.

CASE ANALYSIS

Accident scenario: on 17.01.2015. at 13:35 and on 25.07.2015. at 13:49, in the town of Tavnik near Nova Varos on the curve of the transit route (coordinates 43 ° 49`27``N / 20 ° 35`12``E, altitude of 211 m), the tank vehicle that was transporting 18.6 tons of liquid methyl mercaptan crashed/ overturned.Methyl mercaptan (Methan-ethiol - CH_4S)is a colorless gas, highly poisonous, extremely inflammable and dangerous to the environment, with a strong odor similar to rotten cabbage.

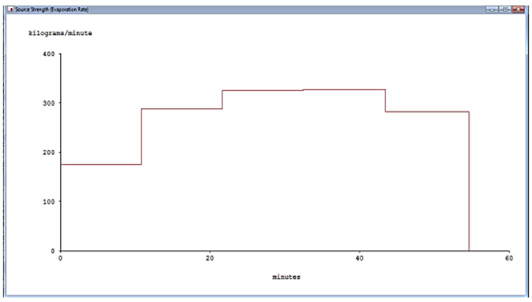
Simulation and analysis of the given accident scenario, in different weather conditions and different seasons in the same geographical area, was done using the Gaussian gas dispersion model, which is commonly used when it comes to the release of liquids or gases.

According to the first scenario, the measured air temperature was -5 ° C, air humidity 25%, cloudiness was 7/10 and wind speed was 7 m / s. During the overturn, an opening of 2 cm in width and 40 cm in length appeared on the body of the tank, 30 cm from the ground.

In the second scenario, the measured current air temperature was + 39 ° C, humidity 75%, cloudiness was 7/10 and northwest wind was blowing at a speed of 3 m / s. During the overturn, on the body of the tank, 30 cm from the ground, an opening of 2 cm in width and 40 cm in length appeared.

The spill pressure was 0.64 atm under the first scenario, ie 1 atm per second. The stability of the atmosphere is determined based on the air temperature profile and wind speed. According to this classification, the class of stability D is in both scenarios (neutral). The maximum amount of the released substance is 327 kg / minute in the first, and 5,200 kg / minute in the second scenario. The total amount of spilled chemicals and the duration of exposure are 15,299 kg in 55 minutes in the first and 16,761 kg in 6 minutes according to the second scenario.

The expressed power of the source (Figure 2) decreases with time, but the concentration on a relatively small surface is significantly increased. Despite the low wind effect, the power of the source is relatively low with a small concentration on a far greater surface.



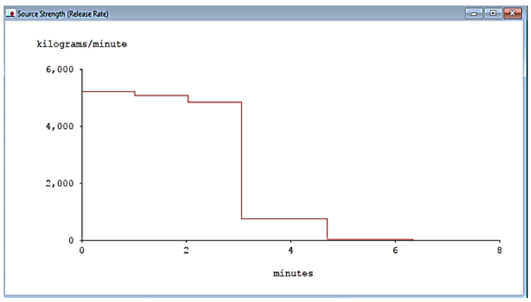


***Figure 2** The power of the source in function of time*

Figure 3 shows the geographical representation of the population's vulnerability on the map of the terrain. Based on software simulation and analysis, ground-based concentrations of pollutants at different distances were calculated for both scenarios. The analysis was done in accordance with the possibilities of the ALOHA program in relation to the integrated application in the ArcGIS tool that was used for modeling and spatial representation of data analysis results.

Different pollution concentrations due to accidents are presented in different colors and refer to a time period of 60 minutes. The area of the largest concentration of pollutants (marked in red) in the first scenario extends to 400 m from the source, and in the second to 3 km. The area of significant pollution (marked with orange) extends to 500 m in the first, or up to 4 km in the second scenario.

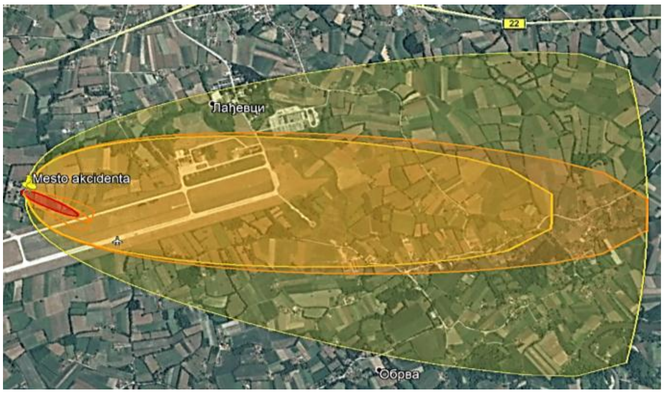


Figure 3 *Geographical representation of the population's vulnerability on the map of the terrain in relation to both scenarios*

The relatively low pollution (indicated in yellow) includes distances up to 600 m in the first, or up to 5 km in the second scenario. All pollution marked in red has serious consequences on the health of all inhabitants. Pollution marked in orange may be a potential problem for certain categories of population such as children, elderly people and chronic heart and lung patients. The population is unlikely to be endangered in areas with a level of pollution marked with yellow.

The maximum concentration of methyl mercaptan is 65.6% (656.317 ppm) in the first scenario, and 100% per second. Chemical pollution concentration limit values are 21.8% (218.000 ppm) for the red area, 13.08% (130.800 ppm) for the orange area and 2.18% for the yellow zone in the first scenario. In the second scenario, the concentration limit is 3.9% (39.000 ppm) for red, 2.34% (23.400 ppm) for orange and 0.39% (3.900 ppm) for the yellow region. Figure 4 presents the vulnerability diagrams for the I and II scenarios.

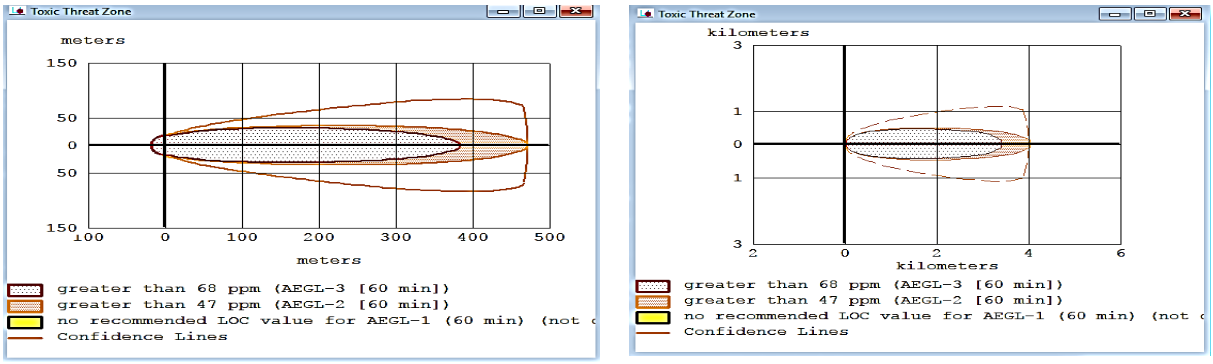


Figure 4 *Population vulnerability diagram for I scenario (left), and II scenario (right)*

According to the first scenario (winter conditions-low temperatures), very high concentrations of pollution due to accidents are observed at a maximum distance of about 500 m in the direction of the wind and the width of the accident area from 100 to 150 m. According to the second scenario (summer conditions - high temperatures), lower concentrations of pollution are noticeable at a maximum distance of about 6 km in the direction of wind and the width of an accidental area of 3 km. Therefore, the potential surface area of the terrain in the first scenario is about 0.075 km^2, while in the other it is about 8 km^2.

CONCLUSION

Chemical accidents can not be predicted in advance and they can lead to very severe consequences as shown with this example with Methyl mercaptan, an extremely toxic gas. The results tell us that the number of victims in the cases described in the simulations would be high if the evacuation did not begin immediately after the occurrence of the accident. From the final results it can be seen that, without a timely reaction, at least 70% of the observed inhabited territory would be exposed to a dangerous dose of a chemical.

Furthermore, the first simulation predicts the formation of a toxic cloud, with a registered increased concentration, which would result in the evacuation of up to 30% of the population in the area. The second simulation points to an increased concentration in the surrounding areas, which would lead to the immediate evacuation of 60% of the population in the area.

It has been shown that the development and application of mathematical modeling and software packages are a modern and necessary field of research. It can contribute to the existing technical analysis of the critical points of the technological process of production, exploitation and transport, to additional risk analysis, prevention of the occurrence and prevention of bad outcomes of the accident.

ACKNOWLEDGEMENT

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THE IMPACT OF THE NEW COPPER SMELTER ON THE AIR QUALITY IN BOR DURING 2016 AND 2017

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Abstract

The paper analyses the impact of the new copper smelter in Bor on the air quality in 2016 and 2017. The period of working of the only new smelter, during 2016 and 2017, was estimated comparing with the standards and comparing with the period before the activating the new smelter, which was represented with the several year period 2010-2014.The degree of reduction in the frequency of exceeding of the limit value (LV)for SO_2 in Bor was determined applying the same procedure as during 2016.The annual SO_2 concentrations in 2016 and 2017, after several decades, were within the acceptable range, below the annual LV for SO_2.There werestill periods with the exceeding of the daily LV concentration of SO_2 in Bor, but the negative trend of their occurrence is encouraging. In the period 2016-2017, the probability of exceeding the LV was 6.3%, which was seven times less than before only the new smelter did operate.

Keywords: Improvement of air quality, New copper smelter, Bor

INTRODUCTION

Monitoring and assessment of the air quality in the Bor region have been specifically assessed using the domestic regulative that is applicable in this area.

According to the Law on Air Protection ("Off. Gazette RS" No. 36/09, 10/13) and Regulation on determination of zones and agglomeration ("Off. Gazette RS" No. 58/11, 98/12 and 105/15), the Bor area is designated as "agglomeration Bor", although it has less than 250000 inhabitants. In accordance with the EU Directive 2008/50/EC, it is done due to the specific problem of the air quality in the area of Bor.

Since the establishment of the national network for the automatic air quality monitoring and started the assessment of the air quality in the zones and agglomerations according to the new regulations, in the agglomeration Bor dominated the III category of the air quality, that is over-polluted air [1,2].Only in the agglomeration Bor, $SO_2$was the pollutant with the dominant influence on the air quality. Therefore, it is understandable that the activation of the new copper smelter in Bor, with significantly lower SO_2 emissions, contributed to the improvement of the air quality in Bor.

The initial impact of the new copper smelter in Bor on the air quality was very positive. This is indicated by the results of the analysis presented in Popović *et al.*[3,4]. In order to continue the monitoring of the state and assessment of improvement, a detailed analysis of the daily concentrations of SO_2 during 2016 and 2017 in Bor was done.

MATERIALS AND METHODS

On the location Gradski Park, within the national network for the automatic air quality monitoring stations (AAQMS) in the Republic of Serbia, AAQMS Bor_Gradski Park starts with operative functioning. It is one of five AAQMS in the Bor area (others are Bor_InstitutRiM, Bor_Brezonik, Bor_Krivelj and recently Bor_Slatina). At this measuring station the most often and the most intensive exceedances of the air quality standards were registered. The exceedanceswere confirmed in 2006 as one of the Europe's maximum daily concentration of SO_2 [5].

Continuous, automatic monitoring of SO_2 is realized with gas analysers SO_2 TELEDYNE API using the reference method - ultraviolet fluorescence, (SRPS EN 14212). Gas analyser calibration is performed at least twice a year, in the calibration laboratory of the Serbian Environmental Protection Agency.

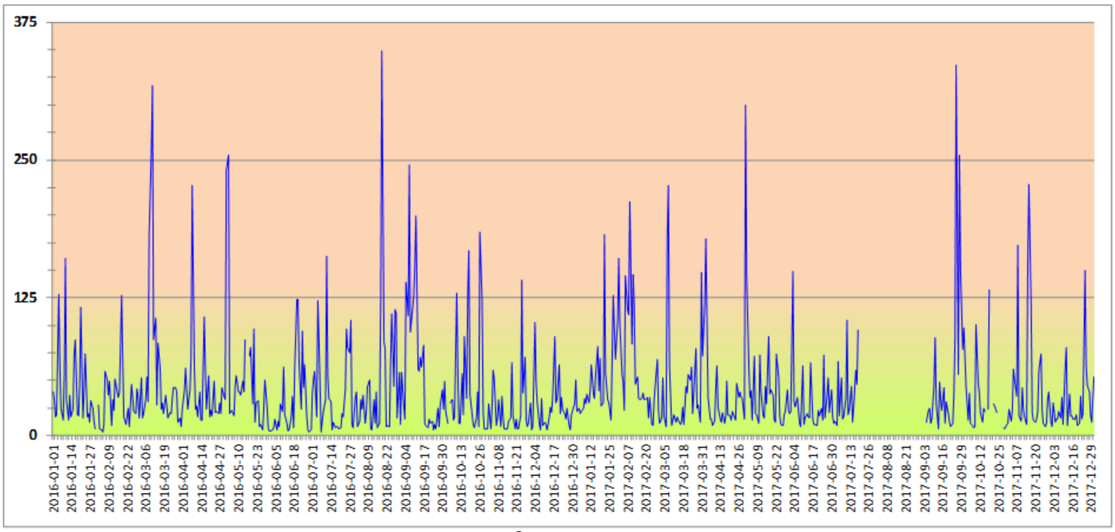

Figure 1 *Daily concentrations of SO_2, µg/m^3, AAQMS Bor_Gradski Park in the period January 2016 - December 2017*

For the analysis daily concentrations of SO_2 from AAQMS Bor_Gradski Park were used. The assessment of the state of the air quality in 2016 and 2017 was done in two ways: the assessment in the relation to the EU air quality standards transposed in the domestic regulation - Regulation for air quality monitoring and air quality requirements ("Official Gazette of RS", No. 11/10, 75/10 and 63/13) and by comparing with the daily concentration of SO_2at the same location in the period 2010-2014.

For this purpose were implemented appropriate data processing to obtain the empirical cumulative distribution of daily SO_2 concentrations at the location Bor_Gradski Park.

RESULTS AND DISCUSSION

Graphic of the empirical cumulative distribution of daily concentrations of SO_2 at the AAQMS Bor_Gradski Park in the period 2010-2014 and in the period of operation of only the new smelter is given in Figure 2. The period of operation of only new smelter is presented by the results of the analysis in two periods; not standard period analysed for the purposes of paper [3] and the two-year period 2016-2017. In that way, it is possible to compare the initial improvement with the next two-year period.

The results of the analyses are used for the assessment of the state of the air quality in Bor compared to the standards and in the relation to the average state before the activating only the new smelter which was presented in the period 2010-2014.

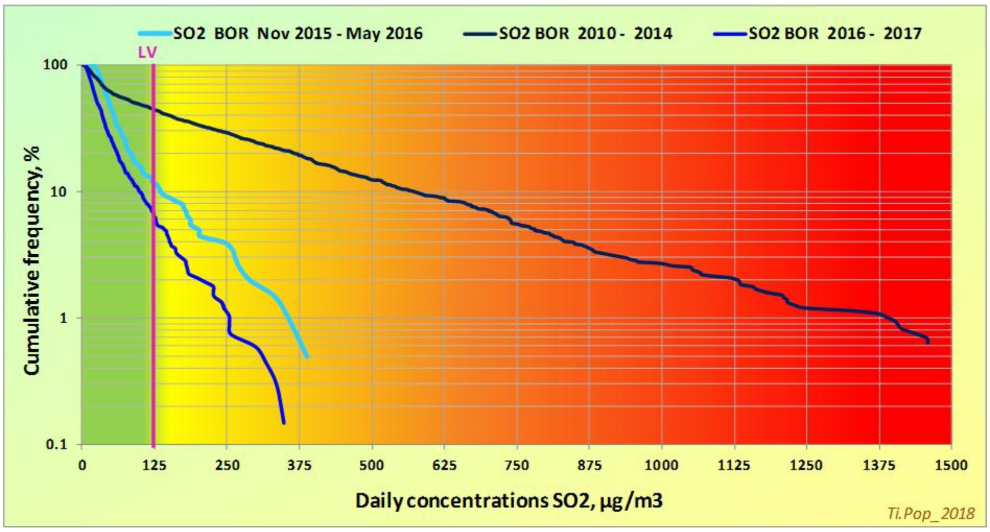

Figure2*Empirical cumulative distribution of the daily concentrations of SO_2 at the AAQMS Bor_Gradski Park in the period 2010-2014, the period of working only new smelter assessed in [3] and the period 2016-2017*

During the period of working only new smelter, starting from November 2015, there were exceedances of the daily LV for SO_2 concentrations, 125 μg/m^3.

According to the data during 2016(availability of data 98.9%) [1], the exceeding of the daily LV was registered for 21 times. The same number of exceedances were recorded in 2017 (data availability 85.2%).

Assessment of the improvement of the air quality in Bor

According to the data and estimates of the annual SO_2 concentrations in 2016 and 2017 were 42.0 and 43.4 μg/m^3, respectively [1]. After many decades, these are the first annual values less than the annual LV for SO_2, which is 50 μg/m^3 (Figure 3). For the first time since 1975 and since the data are available, in 2016 the annual concentration of SO_2 in Bor was within the air quality standard. Therefore, the agglomeration Bor for 2016, according to the current regulations, was classified in the first category of the air quality.

The analysis of the daily concentrations of SO_2 during 2016 and 2017 in Bor indicated the occurrence of the exceeding of the daily LV. What is their frequency, absolute and in comparison with the earlier period, can be seen from Figure 2. More detailed, quantified, the overview and comparison are given in Table 1.

The empirical probability of the occurrence of daily mean concentration of SO_2 greater than 125μg/m^3, which is the value of LV, during the period 2016-2017 was 6.3%.That is seven times less often LV exceeding, P1/P3 (see Table 1), than in period when worked only old smelter! That practically means that in the period of working only new smelter, were seven times less possible occurrence of the polluted air due to the presence of SO_2 according to the EU and domestic regulations.

Analyses of the available data indicated that in the period of operation of the old smelter, the exceeding of the LV could have been several times higher than the allowed [4,6]. The occurrence of such concentrations of SO_2 illustrate the intensity of the LV exceeding. Therefore, in Table 1 are compared the empirical probabilities for the occurrence of daily concentrations that are two, three and 10 times higher than the LV.

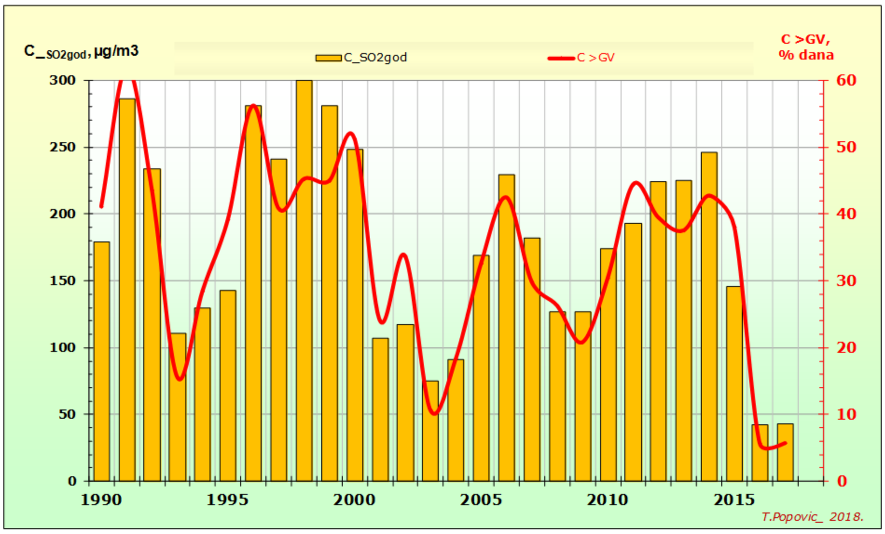

Figure 3 *Annual concentration SO_2 at the location Bor_Gradski Park and percentage of days during the year with exceeding the daily LV in the period 1990-2017*

Table 1 *The empirical probability, in %, of the occurrence of a certain or higher daily concentration of SO_2 at the location AAQMS Bor_Gradski Park*

Daily SO_2 ($\mu g/m^3$)	P1: 2010-2014	P2: Nov2015-May 2016	P3: 2016-2017	P1/P2	P1/P3	P2/P3
125 (1xLV)	44.5	11.5	6.3	3.9	7.1	1.8
250 (2xLV)	29.2	3.9	1.1	7.5	26.5	3.5
375 (3xLV)	19.2	0.5	-	38.4	-	-
1250 (10xLV)	1.2	-	-	-	-	-

LV – limit value; “-“ no data; P1 - the period 2010-2014; P2 – the period of operation of only new smelter [3]; P3 - the period 2016-2017.

The occurrence of the daily values of the concentration of SO_2 at the AAQMS Bor_Gradski Park were greater than 250 $\mu g/m^3$, more than two times the LV, in the period 2010-2014 and had the empirical probability of 29.2%. During the period 2016-2017, there were only few cases where the daily value was more than 250 $\mu g/m^3$.

Their empirical probability of the occurrence was 1.1%. This indicated that the occurrence of two times greater exceeding of the LV, in the period of operation of new smelter was 26 times less often than in the period 2010-2014.

Exceeding the daily concentrations of SO_2 with intensity of three times of the LV and 10 times of the LV, that were in the period 2010-2014 with the empirical probabilities of 19.2% and 1.2%, respectively, were not registered between 2016 and 2017.

This indicated the fact that in addition to a significant reduction of the occurrence of the daily LV exceeding of SO_2 concentration in Bor there was also rapid reduction in the intensity of the LV exceeding.

CONCLUSION

The assessment of the state of the air quality in Bor was carried out in the relation to the standard and in relation to the average state prior to the activation of only the new smelter, which was represented by the period 2010–2014.The positive initial impact of the new copper smelter in Bor on the air quality continued during 2016 and 2017.

The annual SO_2 concentrations in 2016 and 2017 were, after several decades, withinthe acceptable range, below the annual LV for SO_2.There is still the occurrence of exceeding of the daily LV for the SO_2 concentration in Bor, but the negative trend of their occurrence is encouraging.In the period 2016-2017, the probability of the LV exceeding was 6.3%, which was seven times less than before the new smelter.

The intensity of the exceeding the daily LV concentration for $SO_2$was rapidly decreasing.The occurrence of two times greater exceeding of the LV, in the period 2016-2017 was 26 times less often than in the period 2010-2014.

In the coming period, we should maintain and intensify the observed trends in order to reduce SO_2 impact on the air quality in Bor. This implies keeping the annual concentrations below the LV, bringing the frequency of the daily exceedances to the standard acceptable frames and decreasing the frequency of the LV exceedances. That could be the task for the next analysis.

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HAZARDOUS SLUDGE GENERATED DURING WASTEWATER TREATMENT PROCESS

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Abstract
Cleaning of wastewater generated in the autogenous copper smelting process is one of the important environmental issues. This paper deals with the characterization of sludge generated from treatment of metallurgical wastewater which contains heavy metals and arsenic. In accordance with the Legislation of the Republic of Serbia and Council Directive on Hazardous Waste (91/689/EEC) sludge is characterized as hazardous waste. Process of solidification/stabilization (S/S) is considered to be the best available technique for sludge treatment before their disposal.

Keywords: Hazardous waste, Sludge, Wastewater treatment

INTRODUCTION

The effluents generated by the pyrometallurgical copper smelting process usually contain heavy metal ions in concentrations much higher than the permissible levels [1-4]. Due to their high toxicity for humans, animals and plants, wastewaters containing heavy metals are strictly regulated and must be treated before being discharged in the environment [5-8].

Wastewater treatment sludge from a primary copper smelter is characterized as hazardous waste that requires treatment prior to disposal due to its significant contents of heavy metals and arsenic [9,10].

Process of solidification/stabilization (S/S) is considered to be the best available technique for sludge treatment before their disposal [11,12]. It involves mixing a binding reagent with contaminated media or waste, changing the chemical and physical properties of hazardous materials to make it suitable for land disposal.

MATERIAL AND METODS

The pyrometallurgical copper extraction in the New Copper Smelter RTB Bor from sulfide concentrate ($CuFeS_2$, FeS_2, Cu_2S and FeS) is consisted of concentrate drying, autogenous smelting in a flash smelting furnace (FSF) and matte converting process in a Pierce-Smith converter (PSC).

Technological scheme of the New Copper Smelter and off-gas cleaning processes is presented in Figure 1.

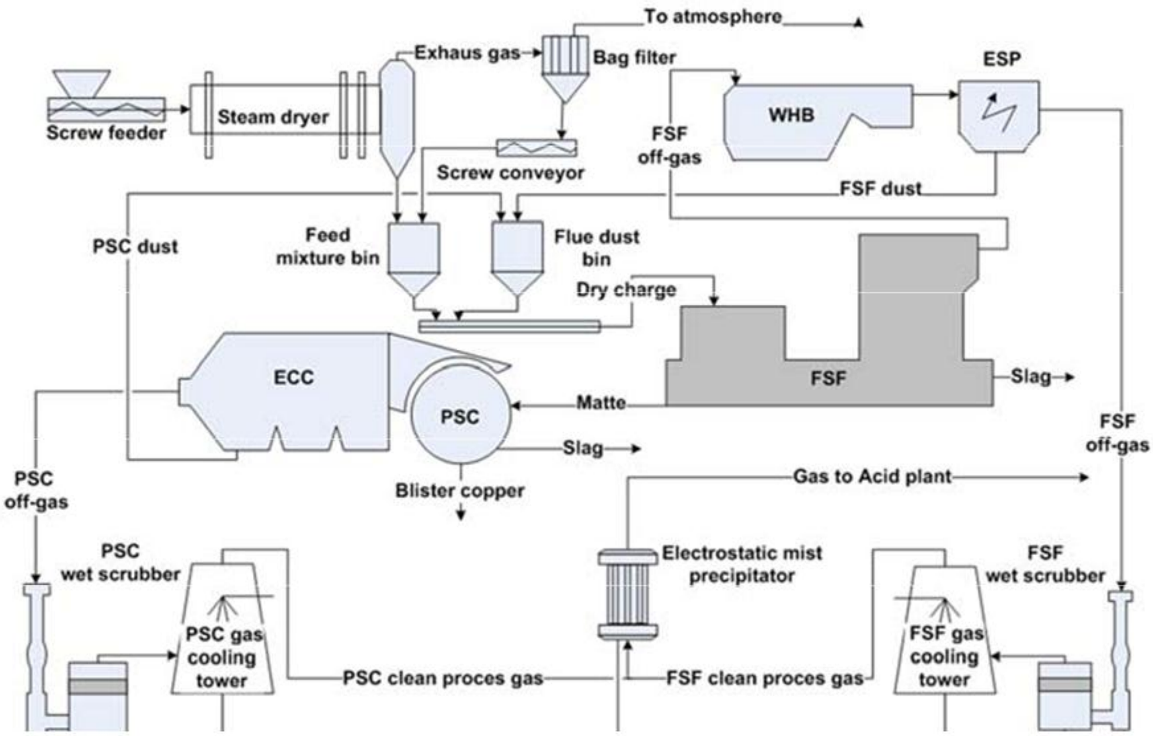

Figure 1 *Technological scheme of the New Copper Smelter and off-gas cleaning process [1]*

Generated weak acid effluents represent wastewaters from the copper smelter that is processed in an effluent treatment plant (ETP). These wastewaters are characterized by a high content in free sulfuric acid and heavy metals such as Cu, Ni, Zn, Fe, Pb, As, Bi, and Sb.

The Effluent Treatment Plant (ETP) is designed to treat contaminated process flows from the copper smelter and converter gas cleaning and cooling operations together with suspension from sulfuric acid plant liquid phase.

In the ETP, the FSF and PSC wastewaters are neutralized with lime while heavy metals are precipitated as hydroxides and from wastewater treatment sludge. The process is conducted in two stages, in four roasters with insertion of calcium(II)hydroxide (slaked lime) as precipitation media. In Figure 2 is presented block technological scheme of the neutralization process.

Outlet flow from the wastewaters treatment plant is the overflow water and sludge. Treated waters are not discharged into the water currents, but are used in the slag flotation technological process.

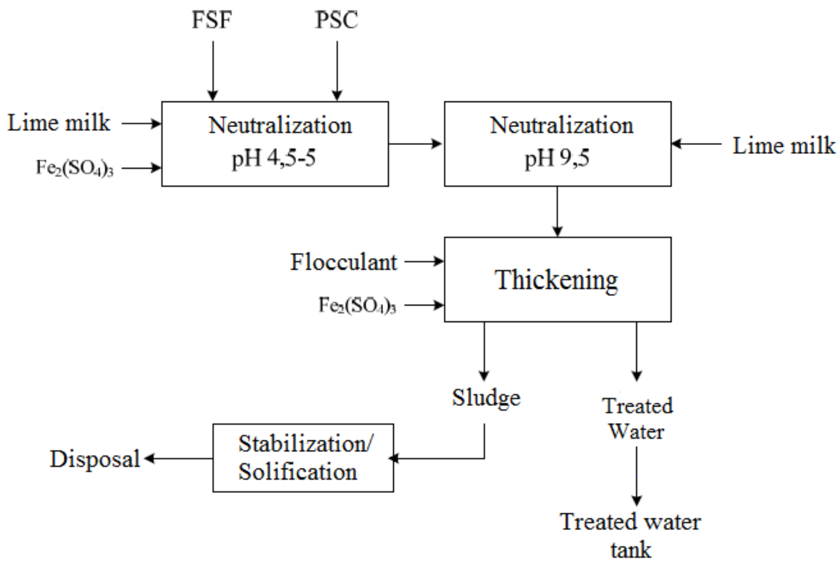

Figure 2 *Block technological scheme of the neutralization process [13]*

Sludge generated from treatment of industrial waste water in the process of primary copper metallurgy has been testing and classificated in accordance with:

- Law on Waste Management („Official Gazette of RS“ no. 36/09, 88/10 and 14/16),
- Regulation on Waste Disposal to the dump yard („Official Gazette of RS“ no. 92/10),
- Council Directive 1999/31/EZ (from 26th of April 1966 on waste dump yards. Official Gazette of European communities I)
- Council Directive on Hazardous Waste (91/689 dated 12th December 1991)
- Commission Decision dated 16th of January 2001, amending Decision 2000/532/EC dated 3rd of May as regards the list of wastes (2001/118/EC).
- Counsel Regulation (EC) No 1195/2006 of 18 July 2006 amending Annex IV to Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants;
- Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC (2003/33/EC)

RESULTS AND DISCUSSION

"MOL" d.o.o. Institute, Stara Pazova, measured the precipitated sludge - solid phase generated from wastewater treatmant plant -" Report on waste testing", October 2015. The result is given in Tables 1-3.

Table 1 *Sample data*

1.	Name of waste: Waste sludge from wastewater treatment plant – solid phase
2.	Location: RTB Bor Group, TIR doo, Cassette landfill with GSP coordinate: N: $44^0$04′38.7″; E: $22^0$06′44.1″
3.	Sampling method: SRPS CEN TR/15310-1,2,3,4,5:2009 (Characterization of waste - Sampling of waste materials - Part 1: Guidance on selection and application of criteria for sampling under various conditions; Part 2: Guidance on sampling techniques; Part 3: Guidance on procedures for sub-sampling in the field; Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery; Part 5: Guidance on the process of defining the sampling plan)

Table 2 *Classification of solid waste generated during the technological process of neutralization*

1.	Waste category, according to the List of waste categories (Q list): **Q9**
2.	Index number of waste according to the Catalogue of waste: **19 08 13*/19 02 05***
3.	Character of the waste: hazardous / not hazardous / inert: **Hazardous waste**
4.	Y labeled according to the List of categories or related types of waste according to their nature or the activity they are creating (Y list): **Y30**
5.	C label according to the List of waste components that make it hazardous: **C8**
6.	H label according to the List of waste characteristics that make it hazardous: **H6**
7.	Sludge is characterized as hazardous waste because of its generic form - in accordance with Council Directive on Hazardous Waste (91/689/EEC), Commission Decision of 16 January 2001 amending Decision 2000/532/EC of 3 May 2000 as regards the list of wastes (2001/118/EC) and the Rule Book on categories, testing and classification of waste "Official Gazette of RS, no. 56/10"; The content of arsenic (As) in the waste increased compared to the reference value according to the List of Waste Constituents with Concentration Limits according to BAGA (The Netherlands Environment Protection Agency), 1997 and the Rule Book on categories, testing and classification of waste "Official Gazette of RS, no. 56/10" - belongs to a dangerous category H6.

Table 3 *Heavy metal concentration (mg kg^{-1})*

Heavy metal content, mg/kg	Measured values	Reference value
Lead, Pb	51.26	5000
Cadmium, Cd	8.76	50
Zinc, Zn	245.13	20000
Copper, Cu	194.61	5000
Chromium, Cr	<8.00	2500
Nickel, Ni	<6.00	5000
Mercury, Hg	<0.13	50(20**)
Arsenic, As	861.68	50

** Concentration values refer to the hazardous characteristic H15.

The reference value is given in accordance with Legislation of the Republic of Serbia and Council Directive on Hazardous Waste (91/689/EEC). The content of arsenic in the waste increased compared to the reference value according to the List of Waste Constituents with Concentration Limits according to BAGA (The Netherlands Environment Protection Agency). Measured value 861.68 mg kg^{-1} is higher than limit value for Arsenic and arsenic compounds which amount 50 mg kg^{-1}.

CONCLUSION

Sludge generated from treatment of metallurgical wastewater is characterized as hazardous waste in the Catalogue of waste within the Rule Book on categories, testing and classification of waste "Official Gazette of RS, no. 56/10" (catalogue number 19 02 05*) and it must be treated before its disposal onto the sludge dump yard.

Process of solidification/stabilization (S/S) is considered to be the best available technique for sludge treatment before their disposal.

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DISTRIBUTION OF 16 US EPA PAHs IN THE SELECTED SEDIMENTS FROM PROTECTED NATURAL RESOURCES OF VOJVODINA (NORTHERN SERBIA)

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Abstract

In order to investigate 16 US EPA PAHs distribution in sediment from protected natural resources of Vojvodina (North Serbia), several methodological approaches were used. Comparison with relevant national and different international regulations values, using diagnostic ratios of specific PAH congenersand quantifying their carcinogenicity potential, were provided novel information of these substances in this part of Pannonian Basin. As outcomes, this research suggests, with accordance with EU, national and regional data results, that dibenzo[*a,h*]*anthracene should be added to the list of priority pollutants within the context of applying the European Water Framework Directive (WFD). The further researches are expected with the special focus on long-term effects on biota and defining possible ways of transformation and complexation with other priority substances.*

Keywords: 16 US EPA PAHs in sediment, Protected natural resources, dibenzo[*a,h*]anthracene, benzo[*a*]pyrene, Substances of concern

INTRODUCTION

Organic pollutants, particularly polycyclic aromatic hydrocarbons (PAHs) represent the ubiquitous environmental pollutants with various structures and varied toxicity generated primarily by a process of thermal decomposition (pyrolysis) and subsequent recombination (pyrosynthesis) of organic molecules [1]. This study has aim to determine the status, level of toxicity and sources of pollution from three protected natural resources of Vojvodina (North Serbia).In accordance with national legislation [2] and European Union Directive recommendations [3], sediments from this area, have been monitored for several group of priority substances such as: heavy metals, organic pollutants and other priority substances [4-11].

The aim of this study is to focus on 16 US EPA priority PAHs (PAH_{16}): naphthalene (Nap), anthracene (Ant), phenanthrene (Phe), fluoranthene (Flur), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*g,h,i*]perylene (BghiP), indeno[*1,2,3-cd*]pyrene (InP), pyrene (Pyr), benzobenzo[*b*]fluoranthene (BbF), dibenzo[*a,h*]anthracene(DahA), acenaphthene (Ace), acenaphthylene (Acy) and fluorine (Flo) in order to examine influences on biota. Several patterns were observed and most carcinogenic substances were selected.

MATERIALS AND METHODS

Sampling sites

In order to ensure the good sampling procedure and uniform spatial distribution of representative samples on the territory of Vojvodina (North Serbia), current investigations included three larger locations from protected natural resources: Gornje Podunavlje, Koviljsko-petrovaradinski rit and Obedska Bara. The six sediment sampling points per sites from G1 toG5, K1 to K5 and O1 to O5, respectively, were selected due to their proximity to various anthropogenic and natural influences. The sampling sites are presented in Figure 1.All sediment samples were collected in the spring and autumn in 2014 and 2015.

Figure 1 *Selected locations of investigated sediments from protected natural resources of Vojvodina (North Serbia): Gornje Podunavlje, Koviljsko-petrovaradinski rit and Obedska Bara*

Sample collection, reagents and standards

The standard sampling procedure was carried out with an Eijkelkamp core sampler on the surface according to the standard method for sediment [12]. Due to the best laboratory practices, after sampling, all samples were split and placed into plastic acid-rinsed boxes (15 × 15 cm and 20-cm deep). The samples were stored at 4ºC and transported to the laboratory for further analysis. All materials used for sampling, treatment and storage of samples and solutions were carefully chosen, acid-cleaned and conditioned to minimize sample contamination [13]. Several procedures were applied for investigate of 16 US EPA priority PAHs (PAH_{16}). All glassware and plastic materials used were previously cleaned by soaking in dilute acid for at least 24 h and rinsed abundantly in deionized water. For EPA PAH_{16} analysis, PAHs standards were purchased from Dr. Ehrenstorfer (PAH-Mix 64 in benzene/dichloromethane = 50/50 at a concentration of 2000 mg L^{-1} for each compound). Phenanthrene-d10 was used as internal standard and was purchased from Supelco (Cat. No. 48094, 2000 μg mL^{-1} in methanol solution).The results were expressed as the mean. The MDL was calculated as 3× STD (standard deviation), while PQL was calculated as 5× MDL.

Data analysis (synthetic sediment multiparameter indicators for PAHs)

The detailed analysis based on results from sediments of three target locations in 2014 and 2015,were done in accordance with several major synthetic multiparameter indicators. First the carcinogenicity of sediment pollution was analysed, using toxic equivalency factor (TEF) methodology[14], which estimates the total carcinogenicity of seven carcinogenic, probable or possible carcinogen PAHs (CANPAHs) [15]relative to benzo[*a*]pyrene and to estimate the total benzo[*a*]pyrene equivalent concentration (B[a]Peq) (Table 1). In Table 3 ratios of fluoranthene to the sum of fluoranthene and pyrene, expressed as Flur/(Flur + Pyr), classify pollution as pyrogenic (>0.4) or petrogenic (0.5 suggesting the combustion of grass, coal or wood) [16]. Other diagnostic combinations of PAH isomers investigated included InP/(InP + BghiP), Ant/(Ant + Phe) and BaA/(BaA + Chr) [17].

RESULTS AND DISCUSSION

Results from the investigated area were compared with the relevant natural, national and different international regulations. Several threshold limit values taken from international sediment quality guidelines (SQGs) taken from Long *et al*. [18] and Macdonald *et al*. [19] were used (Table 1). In order to better understand the effects of processed concentrations of the PAH_{16} it is useful to note that the low-range values (i.e. ERLs or TELs) have adverse effects upon sediment-dwelling fauna and would only be expected infrequently, whereas above the higher ERM and PEL concentrations, adverse effects are likely to occur. In discussion we used mean values in order to indicate the typical value of a set of data.

Table 1 *Concentrations and risk assessment guideline values of PAHs (µg kg^{-1} dry weight) in sediments from three sampling locations of protected natural resources of Vojvodina (North Serbia) with relevant national and different international regulations values*

	Sediment concentrations (µg kg^{-1})									**Comparison data**			
	Koviljsko-Petrovaradinski rit			Gornje podunavlje			Obedska bara			SQG (µg kg^{-1})			
PAHs	**Range**	**Mean**	**RSD (%)**	**Range**	**Mean**	**RSD (%)**	**Range**	**Mean**	**RSD (%)**	**ERL**	**ERM**	**TEL**	**PEL**
Nap	1.8-2.6	**2.2**	18.7	1.8-2.6	**2.2**	18.7	1.8-64.2	**10.2**	157.6	160	2100	34.6	391
Ant	3.1-34	**14.8**	97.9	3.1-4	**3.7**	18.6	0.7-12	**4.1**	64.1	85.3	1100	46.9	245
Phe	11.7-154	**70**	93.1	16.3-17.4	**17**	3.2	6.6-67	**25**	72.1	240	1500	86.7	544
Flur	38.1-366	**172**	82	48.0-63	**57**	12	7.0-168	**33**	131	600	5100	113	149
Flo	3.02-4	**3.4**	20.8	3.02-4	**3.6**	18.6	3.02-13	**3.4**	90.0	19	540	21.20	144
Ace	1.10-1.6	**1.3**	19	1.10-1.6	**1.3**	19	1.10-4.2	**2.5**	31	44	640	5.87	128
Acy	1.89-29	**12.6**	97	1.89-3	**2.3**	19	1.89-7	**2.3**	59	16	500	**6.71**	88.9
Pyr	30.6-292	**136**	83	36.9-55	**45**	19	2.8-65	**19**	103	665	2600	153	1398
BaA	21.80-130	**69**	69	21.70-41	**29**	34	3.14-79	**12**	198	261	1600	74.8	693
Chr	18.80-151	**75**	79.0	23.50-41	**33**	23.9	2.80-81	**18**	133.8	384	2800	108	846
BkF	26.9-89	**53**	50	26.9-53	**40**	29	2.6-88	**20**	72	280	1620	/	/
BaP	27.5-173	**89**	73	28.3-47	**37**	22	3.2-92	**18**	138	430	1600	**88.8**	763
BbF	26.9-89	**53**	50	26.9-53	**40**	29	2.6-88	**19**	134	665	2600	153	1398
BghiP	29.2-197	**99**	77	38.0-58	**45**	23	3.2-88	**18**	128	430	1600	/	/
InP	29.6-71	**47**	38	29.5-63	**41**	42	3.0-65	**19**	103	na	na	/	/
DahA	29.6-71	**47**	38	29.5-63	**41**	42	3.0-65	**18**	116	63.4	260	**6.22**	135
										National values RS 50/2012			
$\sum PAH_{10}$	209-1349	**691**	74	237-388	**303**	23	48-488	**142**	75	10 000	40 000 (remed. values)		
$\sum PAH_{16}$	300-1826	**943**	72	337-566	**435**	24	64-672	**193**	78	/	/	/	/
∑CANPAHs	181-758	**433**	60	187-358	**259**	31	22-458	**95**	112	/	/	/	/
$(\sum CANPAHs/\sum PAH_{16}) \cdot 100$ %	41.5-60.4	**50.5**	16.3	54.7-63.6	**58.8**	6.5	21.7-68.1	**43.6**	28.1	/	/	/	/
∑B[a]Peq	65-269	**153**	60	66-125	**89**	32	7-174	**32**	123	/	/	/	/

Except acenaphthylene(Acy), slightly benzo[*a*]pyrene (BaP) at Koviljsko-petrovaradinski rit and also dibenzo[*a,h*]anthracene (DahA) for all sites higher mean values then TEL all other PAHs have significant to moderate lover than SQGs prescribed values. Also the mean sum of PAH_{10} (142 to 691 µg kg^{-1})and PAH_{16}(193 to 943 µg kg^{-1}) have significantly lesser values than it relevant to Serbian legislation [2] as prescribed 10 000 or 40 000 µg kg^{-1} for remediation values. However, Maliszewska-Kordybach [20] study classified the sum of PAHs as contaminated (from 600 to 1000 µg kg^{-1}). Although the PAHs concentration is not at a higher level, generally, the long-term impact on the biota needs further investigations. Following $\sum PAH_{16}$ distribution in the surface sediment, general graduation can be set: Koviljsko-petrovaradinski rit>Gornje podunavlje>Obedska bara (Table 1), but none of these concentrations imply application of remediation. Based on benzo[*a*]pyrene (BaP) and dibenzo[*a,h*]anthracene (DahA) TEL exceeded values, this concentration should have a minor effect on biota. From point of carcinogenicity the ΣCANPAHs has the same trend as for the sum of PAH_{16}, and also based on distributions of carcinogenic PAHs related to B[*a*]Peq, but ΣCANPAHs has a maximum at Gornje podunavlje(58.8%) and minimum at Obedska bara sampling sites (43.6%).

According to the contribution of the total high carcinogenic PAHs in surface sediments (from 0 to 50-cm depth) from three sampling locations of protected natural resources of Vojvodina (North Serbia) in 2014 and 2015 several facts could be ascertain. Comparing mean values of all locations it is obvious that benzo[*a*]pyrene (BaP) from 41.3 to 53.5% and dibenzo[*a,h*]anthracene (DahA) from 34.7 to 44.6% contribution were dominantly abundantcarcinogenic PAHs in the investigated sediments (Table 2). The same pattern of site distributions for $\sum PAH_{16}$ and PAHs related to B[*a*]Peq were followed by benzo[*a*]pyrene (BaP), while dibenzo[*a,h*]anthracene (DahA) have vice versa distribution.

Table 2 *Contribution of the total high carcinogenic PAHs in surface sediments from three sampling locations of protected natural resources of Vojvodina (North Serbia)*

Contribution of carcinogenic PAHs									
	Koviljsko-petrovaradinski rit			Gornje podunavlje			Obedska bara		
PAHs	Range	Mean	RSD (%)	Range	Mean	RSD (%)	Range	Mean	RSD (%)
BaA	3.34-4.93	**4.24**	16.2	2.99-3.28	**3.18**	4.6	1.26-7.19	**3.58**	48.7
Chr	0.03-0.06	**0.04**	29	0.03-0.05	**0.04**	15	0.01-0.07	**0.04**	46.0
BkF	0.32-0.44	**0.37**	12.9	0.41-0.51	**0.45**	11.8	0.27-0.87	**0.53**	33.7
BaP	41.4-64.2	***53.5***	18.2	37.2-48.9	***42.9***	12.2	15.5-64.3	***41.3***	28.6
BbF	3.18-4.36	**3.71**	12.9	4.07-5.15	**4.47**	11.8	2.12-6.38	**4.06**	27.6
InP	2.51-4.58	**3.47**	25.9	3.86-4.99	**4.45**	11.5	3.67-9.89	**5.86**	35.2
DahA	25.1-45.8	***34.7***	25.8	38.6-49.9	***44.5***	11.3	24.1-70.2	***44.6***	26.0

To detect the sources of PAHs (Table 3), characteristic PAH molecular diagnostic ratios for surface sediments were applied. All mean values from the diagnostic parameters unambiguously refer to pyrogenic sources from grass and coal combustion. Only InP/(InP + BghiP) ratio have values more related to petrogenic, fossil fuel combustion sources at Koviljsko-petrovaradinski rit and Gornje podunavlje. This could be not dominant but more diffuse pollution with possible mixed, associated period with pyrogenic sources. The presence of periodical pyrogenic influences is probably of biomass burning from the nearby agriculture areas of investigated regions and also to a lesser extent coal combustion from the surrounding settlements and industry may cause this spatial distribution of the pollution.

Table 3 *Characteristic PAH molecular diagnostic ratios for surface sediments from three sampling locations of protected natural resources of Vojvodina (North Serbia)*

Molecular diagnosticratio	Koviljsko-petrovaradinski rit			Gornje podunavlje			Obedska bara		
Source parameters	Range	Mean	RSD (%)	Range	Mean	RSD (%)	Range	Mean	RSD (%)
LMW/HMW	0.24-0.47	**0.36**	27.5	0.20-0.30	**0.26**	18.5	0.13-2.81	**0.92**	69.4
Flur/(Flur + Pyr)	0.55-0.58	**0.56**	2.3	0.53-0.58	**0.56**	3.9	0.37-0.83	**0.63**	19.4
InP/(InP + BghiP)	0.26-0.50	**0.37**	28.63	0.44-0.52	**0.46**	9.24	0.36-0.82	**0.58**	24.89
Ant/(Ant + Phe)	0.07-0.23	**0.18**	32.7	0.15-0.21	**0.18**	15.6	0.05-0.32	**0.15**	53.3
BaA/(BaA + Chr)	0.45-0.55	**0.50**	7.8	0.40-0.50	**0.46**	10.4	0.19-0.61	**0.49**	22.5
Total index	7.29	**8.88**	9.0	7.06-8.14	**7.42**	6.4	4.38-10.23	**8.38**	19.0

CONCLUSION

The main intention of this research is to comprehend and improve the national and international understanding of the PAHs sources in similar protected natural resources including improvements to the monitoring design proposed for WFD application, as indicates the necessity of adding additional non priority substance dibenzo[*a*,*h*]anthracene to the future monitoring programs. Also special attention on the impact of the carcinogenic PAHs (e.g. dibenzo[*a*,*h*]anthracene and benzo[*a*]pyrene) on local biota should be investigated due to synergistic effects of pollutants from historical, temporal and bioaccumulation aspects.

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THE CONTENT OF HEAVY METALS AND ARSENIC IN THE SEDIMENTS OF PROTECTED NATURAL RESOURCES OF VOJVODINA (NORTHERN SERBIA)

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Abstract

The aim of this research was to analyse contamination and distribution of seven heavy metals (Ni, Zn, Cd, Cr, Cu, Hg and Pb) and As from sediment of the protected natural resources of Vojvodina (Northern Serbia) in the period 2014 to 2015. Three specific locations were selected: Gornje Podunavlje, Koviljsko-petrovaradinski rit and Obedska Bara. Geo-accumulation index (I_{geo}) and ecological risk factor (ER_i) were used to evaluate the quality of the sediments and determine the potential ecological risks in order to establish pollutants of interest. Hg (0.31-0.39 mg/kg, ER_i round 100), Cr (I_{geo} from 1.04 to 1.13) were identified as heavy metals of concern. The methodology of linear comparison between heavy metal and As concentrations with the relevant natural, national and different international regulations values proved to be insufficient as sediment matrix is more complex category. Solving spatial and temporal influence of diverse sources of pollution need to be employed additional scientific approaches. The remediation and recultivation of extremely sensitive areas is highly important and challenges process, accordingly the reasons and solutions of categorization from sediment quality were proposed.

Keywords: Priority substances, Sediment, Protected natural resources, Hg, Cr

INTRODUCTION

This study aimed to detect the level of heavy-metals and As concentrations in sediment of the protected natural resources of Vojvodina (Northern Serbia). As natural reserves have highly sensitive ecosystems to all the natural (crustal, floods, leaching etc.) and dominantly anthropogenic influences, even sediments from this area are the main sink for these substances. Changing environmental conditions, such as pH, sediment redox potential, etc., sediments can act as a source of metals [1,2]. This study aimed to distinguish the anthropogenic and geogenic influences. The previous studies have shown considerably increased content of organic and inorganic substances in the similar research sites, such as Ludaš Lake [3] and Carska Bara [4], as a result of intense inputs from the human production and consumption activities (industrial, agricultural and transport). In order to carry out an assessment of heavy metal pollution in fluvial sediments, quantitative indexes: geo-accumulation index (I_{geo}) [5] and ecological risk index (RI) [6], which reference the specific regional/local background values are often applied [7,8]. Thus, the oscillations and elevated levels of heavy-metals can easily lead to a conclusion on the possible influences from geological (crustal) sources and anthropogenic contamination in the vicinity of the investigated area and neighbour environment [3,4,9].

Several goals were defined: (1) to obtain monitoring data of inorganic pollutants (Ni, Zn, Cd, Cr, Cu, Pb, Hg and As) in surface sediments, from a sampling campaign which lasted from 2014 to 2015; (2) to explore the degree of geological, anthropogenic and ecological hazards using geological and contamination indices and to gain a complete picture of the pollution in the investigated area of the Pannonian basin with one of the world oldest reservation areas and a natural asset of exceptional value on the UNESCO's list. The obtained results will be valuable for the future activities, including selection of appropriate remediation techniques and/or dredging. These analyses of sediments will additionally facilitate the selection of appropriate criteria in order to evaluate nature natural and distribution patterns of heavy metals and As in this and similar regions.

MATERIALS AND METHODS

Sampling sites and sample collection

The investigations included three locations of the protected natural resources of Vojvodina (Northern Serbia): Gornje Podunavlje, Koviljsko-petrovaradinski rit and Obedska Bara with six sediment sampling points per sites, from G1 to G5, K1 to K5 and O1 to O5 respectively, selected due to their proximity to various anthropogenic and natural influences. The sampling sites are presented in Figure 1. Surface sediment samples were taken from 0 to 0.50 m depth and all sediment samples were collected in the spring and autumn in 2014 and 2015.

***Figure 1** Locations of investigated sediments sites of the protected natural resources of Vojvodina (Northern Serbia): Gornje Podunavlje, Koviljsko-petrovaradinski rit and Obedska Bara*

Sampling was carried out with an Eijkelkamp core sampler on the surface according to the standard method for sediment [10]. Due to the best laboratory practices, immediately after sampling, all samples were split and placed into plastic bags. The samples were stored at 4°C and transported to the laboratory immediately for further analysis. All materials used for sampling, treatment and storage of the samples and solutions were carefully chosen, acid-cleaned and conditioned to minimize sample contamination [11]. Background analyte values were taken from previous papers [3,4].

Physico-chemical analyses

All glassware and plastic materials used were previously cleaned by soaking in dilute acid for at least 24 h and rinsed abundantly in deionized water. For metals analysis, standard solutions were prepared from analytical grade *Suprapur* quality reagents (Merck or J.T.

Baker). For the purpose of the digestion of the sediment samples HNO_3 and HCl *Suprapur* acids were used (Merck). The sediment samples collected were air dried in the accordance with the method ISO 11464:2006 [12]. Samples were then passed through a 250 µm sieve and characterised for the following parameters. For determining the pseudo-total metals content of the investigated sediments, HNO_3 and HCl mixture (3:1) was used for acid digestion in microwave oven Milestone (Stare E microwave) [13]. Sediment extracts were analyzed for Ni, Zn, Cd, Cr, Cu and Pb by flame atomic absorption spectrometry-FAAS (Perkin Elmer, type AAnalyst 700) in accordance with the EPA method 7000b [14]. Arsenic was determined by graphite furnace atomic absorption spectrometry-GFAAS according to the EPA method 7010 [15]. Hg was determined by cold vapour atomic absorption spectrometry (CVAAS) by the modified EN 1483:2007 method [16].

Data analysis

The analysis of heavy metals and As in sediments of three target locations (Gornje Podunavlje, Koviljsko-petrovaradinski rit and Obedska Bara) in 2014 and 2015, were done in the accordance with the several major synthetic multiparameter indicators: geo-accumulation index (I_{geo}) [5] was calculated in order to distinguish geogenic and anthropogenic factors, followed by the potential ecological risk factor (ER_i) as a measure of potential toxicity to biota, and the ecological risk index (RI) [6] presented as the sum of all ER_i for heavy metals in the sediments at each sampling site to gain a complete picture of the complex pollution situation. The derivation of given parameters is given in the detailed explanation of the index in the papers cited above. Background analyte values (S_{back}), sampled from 25 to 50 cm depth, were used from the following location: for Gornje Podunavlje location 10 km east of Ludaš Lake [4], Koviljsko-petrovaradinski rit southeast of Carska Bara at the confluence of the Tamis [3], and Danube rivers and for the Obedska Bara eastern of Sremska Mitrovica [17]. Cadmium range from 0.02 to 0.47 mg/kg and compared to the legislation values [18] was not interesting for the further analysis.

RESULTS AND DISCUSSION

In order to compare the investigated values of heavy metal and As concentrations from all sites from the investigated area with the relevant natural, national and different international regulations, several threshold limit values were observed. Evaluation of potential ecological toxic effects was done comparing the level of investigated parameters to the several other sediment or soil quality guidelines from around the world. The most useful were international sediment quality guidelines (SQGs) taken from Long *et al.* [19], with related levels as threshold effect level (TEL) and probable effect level (PEL) determined by Smith *et al.* [20], effects range low (ERL) and the effects range median (ERM) given by Long *et al.* [19]. In the terms of general categorization, the next conclusion could be drawn. The low-range values (i.e. ERLs or TELs) have adverse effects upon sediment-dwelling fauna and would only be expected infrequently, whereas above the higher ERM and PEL concentrations, adverse effects are likely to occur.

Generally the most values were below the national prescribed criteria from the Serbian legislation [18], categorized as the 0 category (Table 1). Nickel was dominantly in the 0 category, but from the sediment of Obedska Bara it was in the third category implying that sediment was contaminated. This type of sediment is not allowed to be disposed without special protection measures. This sediment should be kept in controlled conditions with the special protection measures in order to prevent the spread of polluting substances into the environment, taking into account the ecological diversity and degree of sensitivity of this protected natural resource. Also, it is possible that Ni content is dominantly crustal origin due to flooding and weathering process from the surrounding Posavina and Fruška Gora mountain region [17], but additional investigation should be carried out.

***Table 1** Comparison between heavy metal and As concentrations (mg/kg) of all sites from the investigated area with relevant natural, national and different international regulation values*

	Sediments from this study			Comparison data						
	Range GP	Range KPR	Range OB	RS 50/2012	RS 50/2012 (remediation values)	ÖNORM S 2088-2	Sediment quality guidelines (SQGs)			
							ERL	ERM	TEL	PEL
Ni	20.2-29.9$^{(0)}$	15.9-22.3$^{(0)}$	72.5-87.6$^{(III)}$	44	210	60	20.9	51.6	18.0	36.0
Zn	129.5-173.3$^{(I)}$	27.6-110.9$^{(0)}$	62.7-110$^{(0)}$	430	720	300	150	410	123.0	315
Cd	0.02-0.03$^{(0)}$	0.03-0.25$^{(0)}$	0.19-0.47$^{(0)}$	6.4	12	1	1.20	9.60	0.60	3.50
Cr	30.0-42.2$^{(0)}$	12.0-23.16$^{(0)}$	41.4-61.5$^{(0)}$	240	380	100	81.0	370	37.3	90.0
Cu	30.2-43.9$^{(II)}$	7.52-27.8$^{(0)}$	28.5-42.0$^{(II)}$	110	190	100	24.0	270	35.7	197
Pb	31.5-39.4$^{(0)}$	6.88-36.0$^{(0)}$	7.64-27.7$^{(0)}$	310	530	100	46.7	218	35.0	91.3
As	14.7-28.3$^{(0)}$	4.16-26.2$^{(0)}$	19.26-37.0$^{(I)}$	42	55	20	8.20	70.0	5.90	17.0
Hg	0.31-0.39$^{(I)}$	0.05-0.24$^{(0)}$	0.14-0.29$^{(0)}$	1.6	10	1.0	0.20	0.70	0.20	0.50

GP - Gornje Podunavlje, KPR - Koviljsko-petrovaradinski rit, OB - Obedska Bara; Values in exponent brackets represent categorisation based on the RS 50/2012 (Limit values for assessing the quality of sediment in sedimentation from the watercourse): 0, I, II, III and IV category, see also Table 1; Criteria for assessing the quality of sediments and permitted methods of treating sediment; ÖNORM S 2088-2 - Austrian Standard.

The degree of metal pollution in the terms of I_{geo} showed the moderately polluted status of this sediment, but interestingly, except Hg with considerable potential ecological risk factor (ER_i), all other heavy metals and As showed low risk to biota (Figure 2b). Only Ni from Obedska Bara sampling site had higher concentration than the limit values of both the Serbian legislation [18] and the Austrian Standard [21]. Concentration of As from all sites had higher level then ÖNORM S 2088-2 prescribed values, but I_{geo} and ER_i impled geogenic origin (Figure 2), which is in the accordance with the previous studies [22,23] due to its characteristic geological origin in Northern Serbia (Vojvodina). I_{geo} values from three locations of Obedska bara had somewhat higher values of Cr (1.04 for O4 and 1.13 for O2) and Ni (1.07 from O6), and also Pb (1.06 for G3 and 1.08 for G4) at Gornje podunavlje (Figure 2a), classifying this sediments as moderate polluted.

Otherwise, except ERM from Sediment Quality Guideline (ISQG), As had higher concentration and impact on biota (Table 1), and Ni from Obedska Bara had higher values then ERM. This oscillation in comparison to the different prescribed values needs additional clarification. Zn had somewhat higher maximum level of 173 mg/kg compared to ERL of 150 mg/kg and TEL of 123 mg/kg at the Gornje podunavlje location. From the same sampling site Cr, Cu, Pb and Hg had higher values than TEL, and Hg also then ERL. Copper from this and the Obedska Bara locations, were in the second category [18] and these maximum values were above ERL and TEL values, but from geological and ecological factors (see Figure 2) Cu had no impact on biota. Lead had only slightly higher value then TEL, but also all other parameters implied natural level of these heavy metals from all sites. Mercury maximum concentrations exceed ERL and TEEL values, and also had potential to harm the biota according to ER_i factor and I_{geo} from the Gornje Podunavlje and Koviljsko-petrovaradinski rit. From aspect of the ecological impact, this metals according to ecological risk factor (ER_i range from 90 to 136, Figure 2) had considerable negative potential in these two locations.

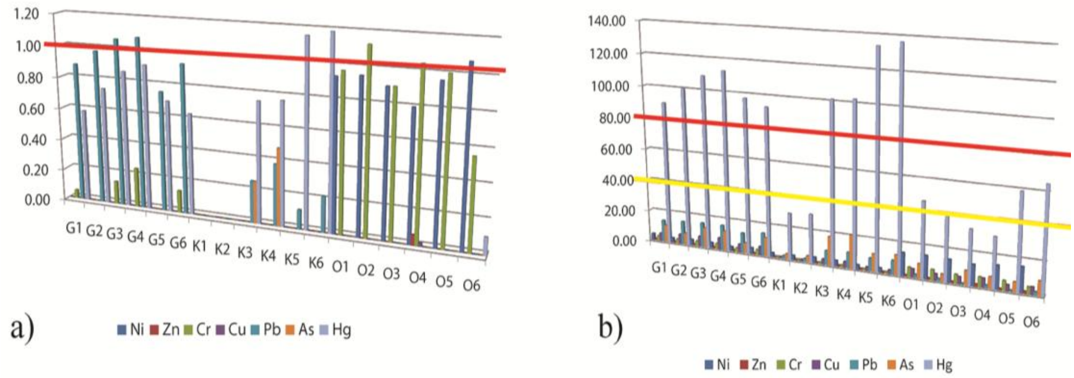

Figure 2 *The degree of heavy metals and As pollution based on all values by sampling sites*
a) I_{geo} plotted with characteristic gradient values (dominantly anhropogenic I_{geo}>1, red colore line);
b) ER_i factor with considerable ecological risk (ER_i >80 red colore line)

After all evaluations dominantly Hg and Cr represented heavy metals of concern, while Ni could have dominantly lithological origin. Pb had slightly higher values then I_{geo} of 1 and no risk to biota according to ER_i values. Based on the location and level of concentration criteria, compared to national and international values, Koviljsko-petrovaradinski rit had the lower ecological status. According to geo and ecological indices, the Obedska Bara had dominantly low risk to biota.

CONCLUSION

The combinations of the prescribed values, geological and ecological indices shifts focus to establish more complex methodology for the analysis of the impact on sediment, not only in the protected natural resources, but also for sediments from other regions. Taking the elements of site specific characteristics of investigated sediments, the most important in risk assessment and categorisation procedures is to implement the wider investigation tools and methods in order to evaluate the sources, type of contamination and impact on biota.

One of the most applicable methods due to determination of metal mobility is sequential extraction. Additional useful techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR), will show the bioavailability of heavy metals and As in the adsorbed, removable and carbonate fractions and potential to migrate in environment dominantly sediment and water matrix.

ACKNOWLEDGEMENT

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FIRST PHASE OF THE BOR RIVER RECLAMATION

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Abstract

The Bor River belongs to a group of rivers where pollution is so great that it does not have an ecosystem. Due to this fact, this river has been subjected to many analyses. However, despite the situation, measures and activities to recover the state of water and surrounding land have not been taken, because the significant investment is needed. For this reason, this paper presents the proposal for the first phase of the Bor River reclamation which includes the adjustment of the watercourse, sedimentation by gravity filtration and recultivation of the surrounding land with minimal investments. After that, the second phase would be realized, that is, the final neutralization of water would be done in an appropriate plant for water treatment, followed by the release of water into the open watercourse, all in accordance with the regulations.

Keywords: The Bor river, Water treatment, Sedimentation, Recultivation

INTRODUCTION

The Bor River is one of the most polluted rivers in Serbia and Europe and there are no living organisms in it (Figure 1).

Its natural state was disturbed by the development of the Bor mine and the settlement of the same name, over a period of more than one century. Bearing in mind that the water from the river eventually flows into the Danube, and further into The Black Sea, this is also an international problem. Therefore, many analyses have been done to meet the need for water treatment, but there is still no effective solution.

Based on previous remarks, a simple procedure for the reclamation of the river is proposed in order to stop the negative trend. The procedure proposes adjustment of the river channel, gravity filtration using a set of four settling basins and recultivation of the surrounding land. After the removal of mechanical impurities whose density is higher than 1 by gravity filtration, there will only remain those whose density is lower than 1, as well as chemical impurities.

Since, as a rule, simple solutions require minimal investment, the process is assessed as economically acceptable.

The next phase of the Bor River reclamation would involve the removal of mechanical impurities whose density is lower than 1 and its chemical neutralization to enable its flow into open watercourses, but it is not described in this paper.

Figure 1 *Bor River (the place where Krivelj River flows into Bor River) [1]*

WATERCOURSES IN BOR AREA

In the area which spreads from Cerovo, via Bor to Zagrađe, the central watercourse belongs to the Krivelj River which flows from the northwest to the southeast, passing on the northeast side of Bor (Figure 2).

On the west side of the open pit Cerovo flows the Valja Mare River, which flows into the Cerovo River that flows on the eastern side of the same pit, thus forming the Kriveljska River. The Kriveljska River flows next to the open pit Veliki Krivelj on the eastern level. On the south of the open pit, Saraka Stream flows into it through the reservoir, as well as the Bor River downstream, which is also redirected by the reservoir. The Krivelj River further flows through the aquifer under the Veliki Krivelj tailing dump, after which it resumes its natural course and flows to Zagrađe where it flows into the Bor River. Relatively close to this place downstream runs The Ravna River, thus forming the Bela River, which flows into the Timok, and it flows into the Danube.

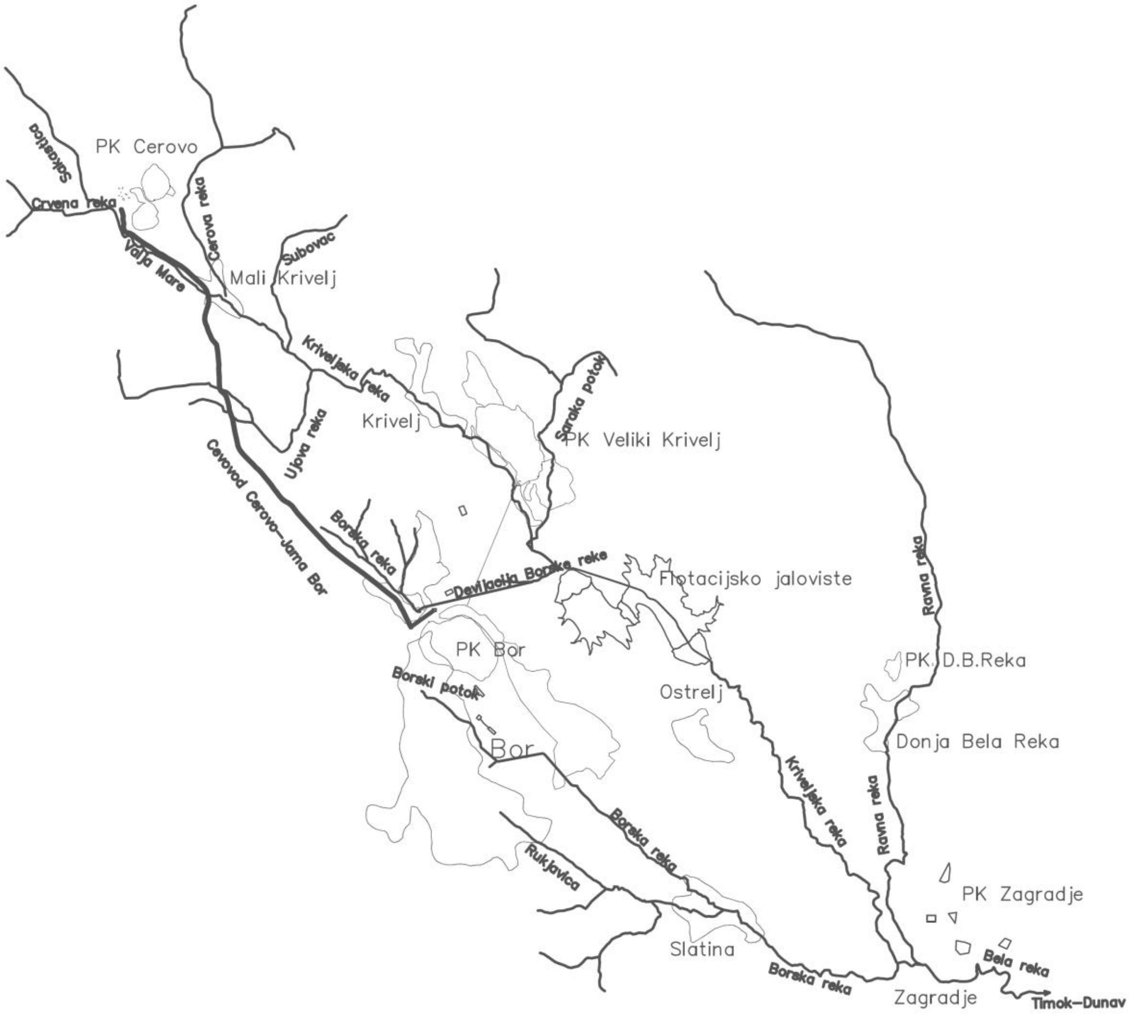

Figure 2 *Watercourses in Bor area*

The natural course of the Bor River was first changed during the World War II when, for the purpose of expanding the open pit in Bor, a reservoir was built, thus moving its course to the east. Further expansion of the open pit in Bor caused its contour line to approach the reservoir, this way creating a problem, or a dilemma, of how to solve the river issue again. This time, a new reservoir was built that redirected the water from the Bor River to the Kriveljska river channel, which meant that the river flow was completely cut off. This means that the river exists in its natural form in the part from its source to the open pit in Bor, where it enters the reservoir, which further means that in this area its flow does not exist because the natural terrain has been significantly changed.

The surface of the open pit in Bor is in fact the industrial area of the RTB Bor Group. On the south side of this area, the river channel is natural in terms of land contour, but water is actually atmospheric water that gravitates towards the industrial area, waste from sewage and waste water from RTB. Due to such water composition, there are no living organism in it, and this is the state of water until the Krivelj River flows into it, that is, until they both flow into the Bela River.

THE BOR RIVER

This paper relates to the part of the Bor River south of the open pit in Bor, i.e. the most polluted one, which consists of the following sections:

- Section 1 from the southern part of the industrial area to the entrance to the village of Slatina,

- Section 2 from the entrance to the village to the end of the village,

- Section 3 from the end of the village of Slatina to Zagrađe.

An overview of the average data on the analyzed part of the Bor River is given in Table 1.

***Table 1** An overview of the average data on the analyzed part of the Bor River*

No.	Section	Length (m)	Width (m)	Inclination (%)
1	I	3 000	50÷150	0.66
2	II	1 500	15÷30	1.33
3	III	4 000	20÷500	0.50
	Total	8 500		

FIRST PHASE OF THE BOR RIVER RECLAMATION

The first phase of the Bor River reclamation includes following activities:

A – Testing the water and shore terrain properties to obtain the initial parameters for further activities.

B – Defining corrected course of the river, which suggests its adjustment where it bends in the flow, especially in the area of Zagrađe where it covers the area of 0.5km in width.

C – Building of service roads is necessary along the entire course of the river in order to establish and access the necessary equipment. Only small portions of land in the village can be excluded because they cannot be approached due to the built constructions. The width of the roads should be 5m in average, while the cross-fall should be considerably less than maximum.

D – Adjusting the river along the corrected course means the formation of a river channel with trapezoidal cross-section and two accompanying embankments, on the left and on the right, with a trapezoidal cross-section as well.

E – Construction of a set of four settling basins for the gravity filtration purposes, measuring 150 m x 50 m x 3 m, should be done in the natural river channel of the Bor River, south of the end of cumulative reservoir under the settlement Bor. The settling basins would be excavated in the river channel and on the shore, and then separated with segmented concrete dams. They would slow down the water enough to allow the sedimentation of the particles with density higher than 1. When the settling basins fill up to 2/3 of their height, they would be cleaned, and the settled material would be deposited to an isolated landfill.

F – After the adjustment of the course and construction of the settling basins, the shore would be recultivated in a standard procedure because it would likely be efficient.

SECOND PHASE OF THE BOR RIVER RECLAMATION

The second phase of the Bor River reclamation would be designed after the realization of the first one, that is, only when its effects would be known. It would include the removal of mechanical impurities whose density is lower than 1 and its chemical neutralization to the prescribed limit in order to enable its flow into open watercourses.

CONCLUSION

This paper describes the first phase of the the Bor River reclamation, which includes the adjustment of its watercourse, gravity filtration in the settling basins and recultivation of the degraded shore.

By adjusting the watercourse, its length would be shortened in the real environment, that is, the shore would have permanent shape.

The main sedimentation would be achieved by gravity filtration in a set of four connected settling basins with concrete dams. The settling basins would be periodically cleaned, and the settled material would be deposited to an isolated landfill.

After the adjustment of the course and construction of the settling basins, the shore would be recultivated in a standard procedure because it would likely be efficient.

After the realization of the first phase of the reclamation and recording of its effects, the second phase would be designed and realized, and it would include water purification in accordance with the regulation.

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SULPHUR DIOXIDE AIR POLLUTION TRENDS IN BOR COMPARED TO SERBIA AND EUROPE

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Abstract

Air monitoring conducted during 2016 and 2017 at different measuring sites in Bor, has indicated that SO_2 concentrations were above the annual limit value (LV). The highest average annual concentration was recorded at the site Jugopetrol, where the daily LV was exceeded the most frequently. The exceeding of daily and annual LVs for SO_2, have indicated that the air quality in Bor during 2016 and 2017 was poor, compared to the air quality in Serbia and Europe. While SO_x emissions in Bor were lower compared to the period from 2010 to 2015, this trend of reduced emission was not noticed for Serbia. The emissions of SO_x in Serbia during 2016 were 20% higher than during 2015. SO_2 concentrations, measured at 15 stations in Serbia, did not exceed the annual LV. In Europe, over the last decades, the emissions of SO_x have decreased by 72%. Reduced emissions of the air pollutants have led to the improvement of the air quality. In Europe, during 2014 and 2015, SO_2 concentrations above the daily LV were registered at five and fours stations, respectively.

Keywords: Sulphur dioxide, Air pollution, Air quality

INTRODUCTION

Air pollution is one of the most important environmental, as well as social problems, which poses multiple challenges. Air pollutants, emitted both from anthropogenic and natural sources, have different impacts on health, ecosystems, environment and the climate [1]. Therefore, monitoring and improving of the air quality are of particular importance [2]. One of the most important air pollutants is sulphur dioxide (SO_2) [1]. The processes of smelting of sulphide ores and burning of fossil fuels represent one of the dominant sources of SO_2 [3]. SO_2 can persist in the air for a few hours or a few days, and due to the transformation processes in the air, it can cause acidification of the atmosphere and the apparition of acid rain [2]. Besides, the deposition of atmospheric sulphur compounds leads to acidifications of soils and freshwater, and affects biodiversity. On the other hand, acidification may lead to increase of mobility of heavy metals present in soils and water, thus increasing the risk of their uptake in the food chain [1].

The aim of this paper is to present the concentrations of SO_2 in Bor during 2016 and 2017, and compare it to corresponding air quality in Serbia and Europe.

MATERIALS AND METHODS

Mining and pyrometallurgical copper production are the most important pollution sources in Bor [3]. Due to the high air pollution, the concentrations of SO_2 in the air are measured at sites located in different zones in Bor. The monitoring of SO_2 during 2016 and 2017 at measuring sites (Table 1) was performed by the Mining and Metallurgy Institute Bor [4].

Table 1 *Description of the measuring sites [4]*

Measuring sites	Zone	Geographic coordinates	Altitude
Jugopetrol (JP)	Suburban/industrial	N 44º03’15.36’’ E 22º07’46.43’’	363 m
Technical Faculty (TF)	Urban/industrial	N 44º04’54.45’’ E 22º05’42.52’’	404 m
Institute (IN)	Urban	N 44º03’35.72’’ E 22º06’05.16’’	386 m
Slatina (SL)	Suburban/industrial	N 44º02’25.76’’ E 22º09’47.51’’	234 m
Town Park (TP)	Urban	N 44º04’33.51’’ E 22º05’58.16’’	378 m

RESULTS AND DISCUSSION

Air quality in Bor

According to the Serbian Regulation [6], the annual limit value (LV) for SO_2 concentration is 50 μg m^{-3}. The average annual SO_2 concentrations were above the annual LV at the sites JP, TF and TP during 2016 and 2017 (Figure 1). Although the average annual SO_2 concentrations were above the LV, this exceeding were not pronounced during previous years. This can be observed as an improvement in the air quality, compared to the period from 2009 to 2015, when the average annual SO_2 concentrations were constantly and considerably above the LV, except at the site Brezonik during 2009 [5]. In the period from 2005 to 2008 the average annual SO_2 concentrations at the site TP were: 169, 238, 175 and 112 μg m^{-3} [7]. At the site JP, in the same period, SO_2 concentrations on an annual level were: 215, 199, 189 and 177 μg m^{-3}, while at the site IN: 49, 86, 82 and 71 μg m^{-3}, respectively [7].

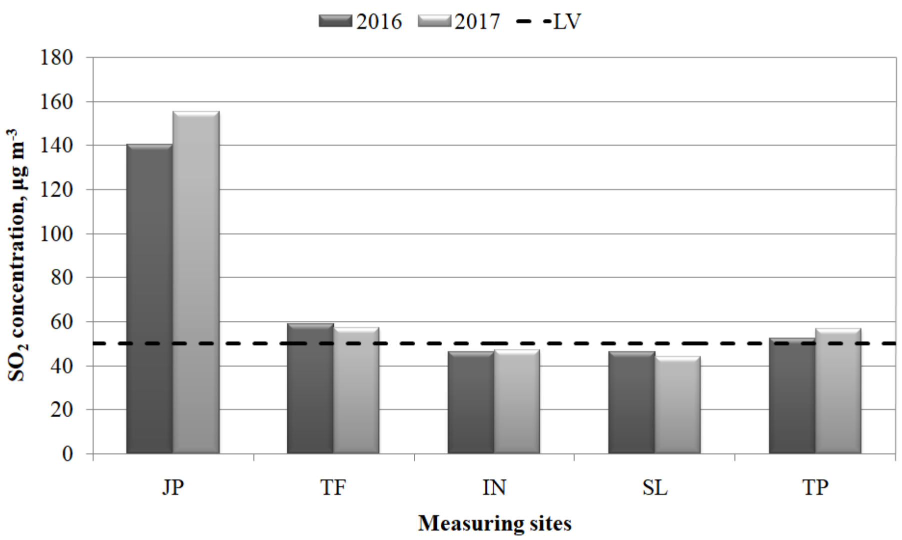

Figure 1 *The average annual SO_2 concentrations (μg m^{-3}) at different measuring sites (Dashed line – limit value (LV) according to the Serbian Regulation [6])*

The number of days when measured SO_2 concentrations were above the daily LV, according to the Serbian [6] and European [8] Regulations, are shown in Table 2.

Table 2 *The number of days above the daily LV (125 µg m^{-3})^{a,b}*

Measuring sites	2016	2017
Jugopetrol	119	94
Technical Faculty	17	17
Institute	3	4
Slatina	10	5
Town Park	17	12

[a] Serbian Regulation [6]; [b] EU Regulation [8].

Compared to the period from 2009 to 2015, the number of exceedings of daily LV for SO_2 were lesser. During 2014, a maximum of exceedances of the daily LV was recorded, amounted: 178 (for the measuring site IN), 245 (TP and JP), 312 (TF) and 165 (SL) [9]. At the site TP, during 2005, 2006 and 2007, the number of days above the LV was 119, 155 and 109, respectively. Until April 2010, the LV for daily SO_2 concentrations was 150 µg m^{-3} [10].

Air quality in Serbia

In the period from 2011 to 2015 electrical energy and heat production have contributed with 95-96% to SO_x emissions. Industry sector and other stationary combustion have contributed with 2-3%, while the contribution of the rest of the sectors was negligible [11].

During 2016, the emission of SO_x in the air was 388.34 Gg, which is 20% higher than during 2015 in Serbia [11]. Spatial distribution of SO_x emissions in Serbia during 2016 is shown in Figure 2.

Compared to the SO_x emissions during previous years (10,000–50,000 t per year during 2010; 50,000–10,000 during 2011; 1,000–50,000 in 2012; 2013 and 2014; 100–1,000 during 2015) [12], the emissions in Bor during 2016 were the same as in 2015, and amounted 100–1,000 t per year.

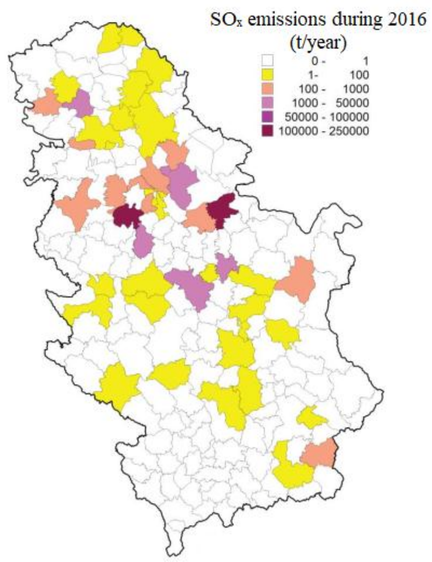

Figure 2 *Spatial distribution of SO_x emissions (t per year) during 2016 in Serbia [11]*

Monitoring of SO_2 concentrations in the air in Serbia during 2016 was performed at 15 measuring stations. The average annual SO_2 concentrations were in the range from 7 to 41 μg m^{-3}, and were below the annual LV according to the Serbian Regulation. The daily LV was exceeded only for one day at one measuring station in Belgrade [11].

Air quality in Europe

Over the last decades, the environmental policies have contributed in reducing emissions of air pollutants and have resulted in considerable improvement of the air quality in Europe [13]. As stated in the report from the European Environment Agency (EEA) [1], reduced emissions have led to the improvement of the air quality. However, a large proportion of population in Europe is still exposed to air pollution that exceeds the EU standards and the World Health Organization Air Quality Guideline (WHO AQG), amounting 20 μg m^{-3} [14].

The exposure of urban population of Europe to SO_2 concentrations above the daily limit has decreased over the past decades. In 2000, 85% of the EU-28 urban population (28 Member States of the European Union) was exposed to SO_2 concentrations above the WHO AQG [1]. During 2014 and 2015 the EU-28 urban population was not exposed to SO_2 concentrations above the EU daily limit, however, 38% (during 2014) and 20% (during 2015) of this population was exposed to SO_2 concentrations exceeding the WHO AQG [1,13].

Compared to other air pollutants, in the period from 2000 to 2015, the largest decrease in emissions of 72% was noticed for SO_x (Figure 3) [15].

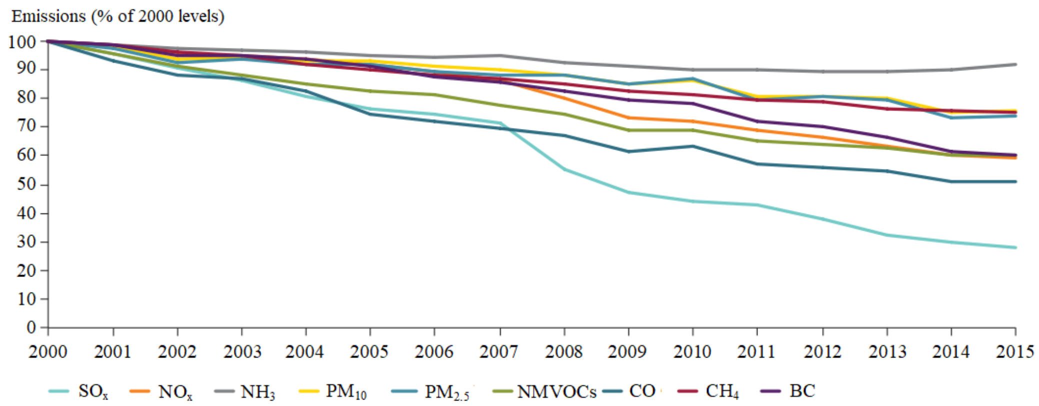

***Figure 3** Emissions of different air pollutants in EU-28 from 2000 to 2015 [15] (NMVOCs – Non-methane volatile organic compounds, BC – Black carbon)*

The reduction in SO_x emissions in Europe in the period from 1990 to 2015 for different sectors is shown in Figure 4.

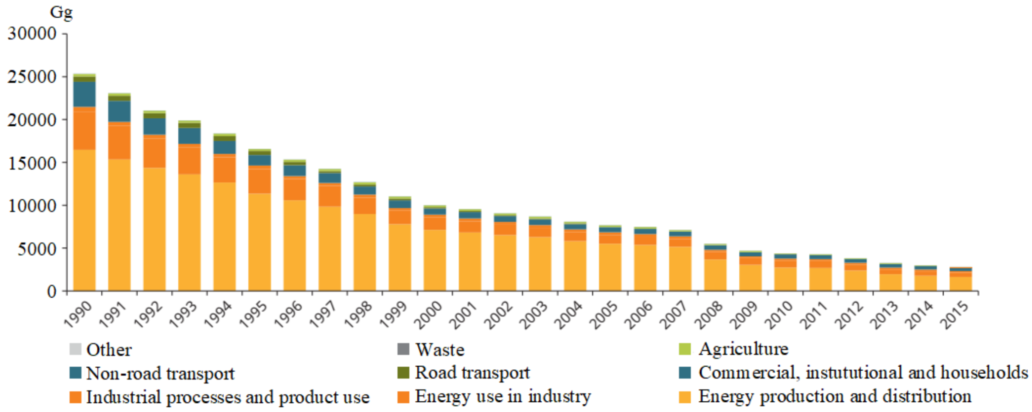

Figure 4 *Emissions of SO_x by different sectors in the EU-28 [15]*

In Europe, the main anthropogenic sources of SO_x are stationary power generation, industry and commercial, institutional and household fuel combustion. As it can be seen from Figure 5, the largest contributor to total SO_x emissions in 2015, contributing with nearly 60%, was energy production and distribution sector [1].

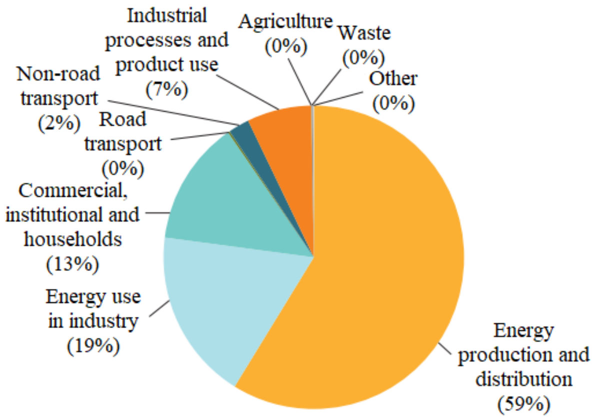

Figure 5 *SO_x emissions in the EU-28 in 2015 by sectors [15]*

During 2014, SO_2 concentrations above the daily LV were registered at four monitoring stations in Iceland, because of volcanic eruption, and at one measuring station in Bulgaria out of 1350 stations in 34 European countries [13]. According to the EEA [1], during 2015 SO_2 concentrations exceeding the daily LV were registered at four stations out of 1322 stations in 37 European countries. The SO_2 concentrations have exceeded the WHO AQG for daily mean concentrations during 2015 at 30% of all the stations.

CONCLUSION

The concentrations of SO_2 measured at different sites in Bor during 2016 and 2017 were presented in this paper. The average annual LV was exceeded at almost all the sites, while the exceedings of the daily LV were frequent. Compared to previous years, the average annual SO_2 concentrations were lower, and the number of exceedings of the daily LV was smaller. The SO_2 concentrations on an annual basis measured at 15 stations in Serbia did not exceed the LV. Although the emissions of SO_x in Serbia were higher during 2016 compared to 2015, the emissions in Bor were lower during 2016 compared to the period from 2010 to 2015. In

Europe, the environmental policies have contributed to reduced emissions of air pollutants which contributed to significant improvement of the air quality. In the period from 2000 to 2015, the reduction of SO_x emissions amounted 72%. During 2014 and 2015, the exceedings of the daily LV were negligible since the SO_2 concentrations higher than 125 μg m^{-3} were registered at few of more than 1300 stations in Europe. The exceeding of daily and annual LV given for SO_2 concentrations at measuring sites in Bor, compared to the air quality in Serbia and in Europe, indicated that air quality in Bor during 2016 and 2017 was poor.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (III46010 and TR33038). Our thanks go to Professor Mara Ž. Manzalović from the Technical Faculty in Bor, for providing language assistance.

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THE AIR QUALITY ASSESSMENT IN THE BOR AGGLOMERATION IN THE PERIOD 2010–2015

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Abstract

The air quality of the Bor agglomeration was assessed in the period 2010-2015. According to the proposed classes of air quality by the Serbian Environmental Protection Agency, the air was mostly "very polluted", primarily with SO_2 based on the average daily concentrations. Based on the annual concentrations of SO_2, the air was of third category, since the defined tolerant value was exceeded in 6-year period.

Keywords: Air pollution, Air quality, SEPA, SO_2, PM_{10}

INTRODUCTION

Mining–metallurgical operations, beyond the benefits that arise from metal production, are known for creating considerable environmental problems to the surrounding area, by emitting polluting substances into soil, water and the air, therefore polluting them. In such polluted environments, all the living organisms are endangered because of disruption of the natural balances.

Particulate matter (PM) pose a great risk to humans, not only because their chemical composition (which is often toxic or cancerous), but because of their size, since the ultrafine PM (<0.1 μm) could reach alveolus by inhalation from the polluted air. According to the World Health Organisation (WHO), severe health effects could arise in population exposed to air pollution, from subclinical (subtle) effects and impaired pulmonary function to premature mortality [1].

MATERIALS AND METHODS

The Serbian Environmental Protection Agency (SEPA), as national institution, is obligated to collect, update and process the results of the air quality monitoring from the national network of automatic measuring stations, for the purposes of reporting on the national and the European Union level. The legal basis in Serbia is regulated by the Law on Air Protection and bylaws [2]. The establishment of national system of the Automatic Air Quality Monitoring Stations (AAQMS) started in Bor and Smederevo during 2006. Preparatory activities and much of the project was implemented in the period 2008-2010, and it was completed during 2011. By fulfilling the obligations of informing the public about the air quality, the SEPA presents the results of automatic air quality monitoring in real time. However, these are preliminary, unverified values of air quality parameters. Verified values and assessment of air quality in Serbia are given in the Annual Reports on the air quality status, which are also available online [2].

According to the Serbian Regulation, the limit (LV) and tolerant (TV) values are proposed for SO_2 and PM_{10} per hour, day or calendar year [3]. Compared to the WHO guidelines [4], 24-hour LV for SO_2 are much higher in the Serbian Regulation. Regarding PM_{10}, 24-hour LVs are uniform in both regulations, but higher for the 1–year period in the Serbian (Table 1).

Table 1 *Air quality guidelines (in μg/m³) for the purposes of the protection of human health according to the Serbian Regulation [3] and WHO guidelines [4]*

Pollutant	**Averaging period**	**Limit value (LV)**	**Exceedance of LV**[b]	**Tolerant value (TV)**	**Limit of assessment**[c]		**AQG**[d]
					Lower	**Upper**	
SO_2	1 h	350	24 times	500	/	/	/
	24 h	125	3 times	125	50	75	20
	year	50	/	50	/	/	/
PM_{10}[a]	24 h	50	35 times	75	25	35	50
	year	40	/	48	20	28	20

[a] particles less than 10 μm in diameter; [b] LV cannot be exceeded during one calendar year; [c] needed for the calculation of the Serbian Air Quality Index; [d] Air quality guidelines according to the WHO; TV - limit value + tolerance limit; / not defined.

The Serbian Air Quality Index (SAQI) is used for the air quality assessment (Table 2) and it is based on the frequencies of numerical concentrations of the pollutants given in five classes for daily or annual averaging periods (Table 3) [5]. There is another classification of air quality in three categories (Table 4) based on the annual average concentrations of polluting substances, also defined by the SEPA [5].

Table 2 *Definition of the air quality classes by the Serbian Air Quality Index (SAQI) [5]*

EXCELLENT	When polluting substance is not detected or it is present in concentrations which are below the lower limit of assessment.
GOOD	When the concentration of polluting substance is between the lower and upper limit of assessment.
ACCEPTABLE	When the concentration of polluting substance is higher than the upper limit of assessment but still below the limit value.
POLLUTED	When the concentration of polluting substance is between the limit and tolerant value.
VERY POLLUTED	When the concentration of polluting substance is higher than the tolerant value.

Table 3 *Determination of the air quality classes of the Serbian Air Quality Index [5]*

Period	**Pollutant**	**Excelent**	**Good**	**Acceptable**	**Polluted**	**Very polluted**
24 h	SO_2	0.0–50.0	50.1–75.0	75.1–125.0	125.1–*187.5*	> *187.5*
	PM_{10}	0.0–25.0	25.1–35.0	35.1–50.0	50.1–75.0	> 75.0
Calendar year	SO_2	0.0–30.0	30.1–40.0	40.1–50.0	50.1–*75.0*	> *75.0*
	PM_{10}	0.0–20.0	20.1–28.0	28.1–40.0	40.1–48.0	> 48.0

Underlined concentrations obtained by the interpolation of the corresponding LVs and TVs; the values shown in italic represent 50% higher values than the TVs since the LV and TV are the same for SO_2 on a daily and an annual level.

***Table 4** Definition of the categories of the air quality [5]*

First category	Unpolluted or slightly polluted air where none of the LVs were exceeded.
Second category	Moderatly polluted air where the LVs are exceeded for one or more pollutants.
Third category	Very polluted air where the TVs are exceeded for one or more pollutants.

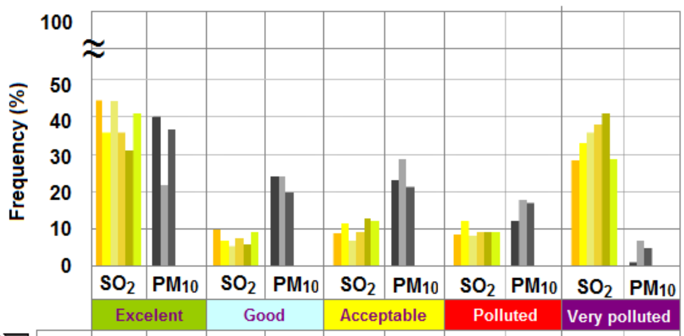
RESULTS AND DISCUSSION

The main polluting substances in the Bor area are SO_2 and PM rich in Cu and other accompanying metals and metalloids, of which the greatest risk comes from arsenic. These harmful elements originate from raw materials – sulphide copper ores (such as chalcopyrite $CuFeS_2$, chalcosine Cu_2S and coveline CuS). The “old” sulphuric acid plant (production of sulphuric acid from SO_2) could process less than 60% of the waste gasses, while the rest of the gasses were discharged untreated into the atmosphere of Bor [6]. Despite the dust removal from waste gases in three stages by electro–filters [7], PM was still reaching the air along with the unutilized SO_2. The main pollution sources in the Bor area, beside the “old” copper smelter, are flotation–tailing ponds and overburden dumps, from which fugitive dust are emitted to the surrounding area, mainly used for agricultural purposes. For many years, the town of Bor was considered as “environmental black point” not only in Serbia, but in Europe as well. Since the outdated technology (approximately 50 years old) was one of the main reasons of the poor air quality of the Bor area, new copper smelter and sulphuric acid plant were constructed near the old ones. During the course of 2016, after a short running–in period, new facilities were in use [6-8].

The Bor agglomeration (two or more stations on the territory of a municipality) is consisted of four measuring stations: Town Park, Institute, Brezonik and Slatina. All the stations are implemented for the measuring of industrial type of pollution according to the SEPA. Although two of them are situated in suburban and rural zones, their purpose is also monitoring the pollution from the copper smelter due to negative influence of wind rose of the area [5].

As can be seen from Figure 1, based on the average daily SO_2 concentrations, the air quality in the Bor agglomeration was mainly between “excellent” and “very polluted” since these two categories were represented each by 30% or more in the period 2010–2015. The air quality classes “good”, “acceptable” and “polluted” were represented each by about 10% of the whole data set. There is no available data for PM_{10} after 2013 for the Bor agglomeration (Figure 2). However, by comparing the data from 2010 and 2012, the decline of the PM_{10} frequencies within “very polluted” category could be noticed. In the 3–year presented period, regarding PM_{10}, the air quality in the Bor agglomeration was mainly “excellent”, “good” and “acceptable”.

In Figure 2, estimated emissions of SO_x (mainly SO_2) and PM_{10} are presented for the Bor agglomeration during 2015. According to the air pollution data, emissions of SO_x were in the range of 100–1,000 t, while emissions of PM_{10} were between 30 and 50 t. The estimated emissions for these two pollutants were the lowest during 2015 compared to the period from 2010 to 2014 (Table 5). During 2011, 2012 and 2013, emissions were estimated to be the highest.



	SO2	PM10	SO2	PM10	SO2	PM10	SO2	PM10	SO2	PM10
	Excelent		Good		Acceptable		Polluted		Very polluted	
2010	44	40	10	24	9	23	8	12	28	1
2011	36	22	7	24	12	29	12	18	33	7
2012	44	37	5	20	7	21	8	17	36	5
2013	36	/	8	/	9	/	9	/	38	/
2014	31	/	6	/	13	/	9	/	41	/
2015	41	/	9	/	12	/	9	/	29	/

and "/" no data

Figure 1 *Assessment of the air quality in the Bor agglomeration for the period 2010–2015 (the frequency of the certain class according to the SAQI on a daily averaging periods for SO_2 and PM_{10}) [5,9–13]*

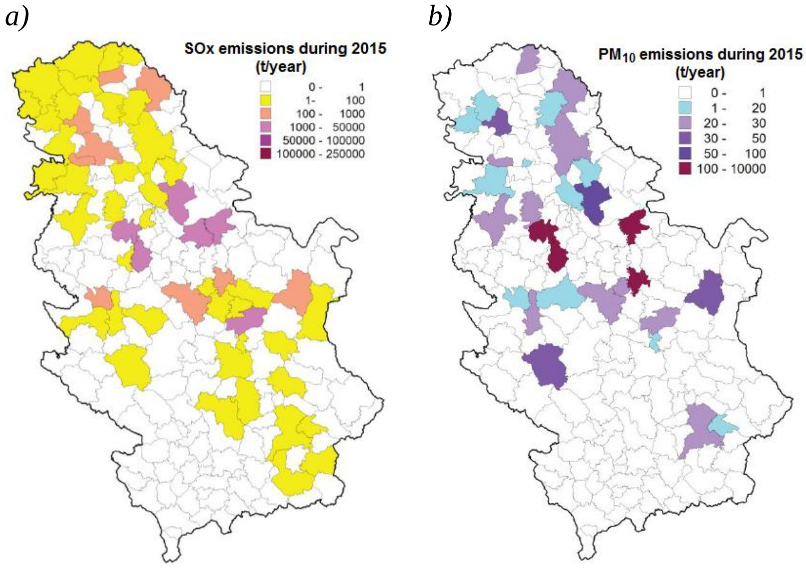


Figure 2 *Estimated emissions (t/year) of SO_x (a) and PM_{10} (b) during 2015 in Serbia [5]*

Table 5 *Estimated emissions of SO_x and PM_{10} (t/year) in the Bor agglomeration in the period 2010-2014 [9–13]*

Pollutant	2010	2011	2012	2013	2014
SO_x	10,000–50,000	50,000–100,000	1,000–50,000	1,000–50,000	1,000–50,000
PM_{10}	500–1,000	100–10,000	100–10,000	100–10,000	100–1,000

At the station Town Park, which is one of the stations in the Bor agglomeration, located in close vicinity of the copper smelter, percentage of the valid data for SO_2 was very high during 6–year period (Table 6), therefore the assessment of the air quality of the area around the station Town Park was fully representative.

Table 6 *The availability of the daily SO_2 concentrations in the period 2010–2015 at the station Town Park in the Bor agglomeration [5,9-13]*

Availability od data (%)	2010	2011	2012	2013	2014	2015
Town Park	83%	98%	90%	79%	86%	99%

As mentioned before, the air quality could be also assessed based on the average annual concentrations of pollutants. During 2015, the air quality in the Bor agglomeration was of the third category (Figure 3). It means that air was "very polluted", since the TVs were exceeded for one or more pollutants. This evaluation was made based on the SO_2 annual concentration which exceeded the TV (Table 4). At the station Town Park, during the presented 6–year period, the air quality was also of the third category, based on the average annual SO_2 concentrations (Table 7). It could be also seen that the number of days in which the LV for SO_2 was exceeded was also very high during 6–year period.

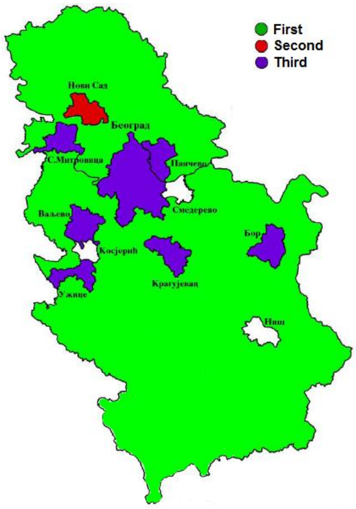


Figure 3 *The air quality evaluation in Serbia based on the annual average SO_2 concentration during 2015 [5]*

Table 7 *The air quality trends for SO_2 at the station Town Park in the Bor agglomeration in the period 2010–2015 [5,9–13]*

Parameter	2010	2011	2012	2013	2014	2015
SO_2 (μg/m^3)[a]	174	193	224	225	246	145
Number of exceedances of LV[b]	111	162	144	137	156	139
Category[c]	Third	Third	Third	Third	Third	Third

[a] the annual average SO_2 concentration; [b] the number of exceedances of the daily LV for SO_2 during a calendar year; [c] based on the average annual SO_2 concentration.

CONCLUSION

The air quality of the Bor agglomeration was clearly related to the pyrometallurgical production of copper from sulphide ores which represented the primary source of pollution. Due to outdated technology and inefficient dust removal from the waste gases, large quantities of SO_2 and PM_{10} were discharged into the atmosphere of Bor. During the presented 6–year period, the air quality in the Bor agglomeration was considerably polluted with SO_2

according to the Serbian Air Quality Index. Also, based on the annual average concentrations of SO_2, the air quality was of the third category in the period 2010–2015, since the proposed TV for SO_2 was greatly exceeded.

During a short period, after 2016, the new copper smelter and sulphuric acid plant have justified their implementation since the reduction of the air pollution is notable. Benefits for the environment are yet to be seen.

ACKNOWLEDGEMENT

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OVER 120 YEARS OF ORNITHOLOGICAL RESEARCH IN THE IBA AREA ZASAVICA

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Abstract

The first data on the fauna of the birds of Zasavica is given by Josif Pančić [5] . The first details are given by the brothers Ernest and Robert Dombrovski about the bird fauna of the birds of Zasavica and the whole north Macva, listing 203 species. In the period of more than 120 years in the area of today's IBA Zasavica, 215 species of birds. Birds species have undergone significant changes, primarily due to anthropogenic activity and drastic changes in habitat due to drying and shrinkage to increase arable land. Many species of birds at the end of the nineteenth century have, in modern times, changed nesting status and are now regular or casual on migration and wandering or wintering. In the Zasavica area, six species have the status SPEC 1, and in two breeding species (A.nyroca and H.albicilla), the number exceeds 1% of national populations. Zasavica for some species is one of the few remaining nesting habitats in northwestern Macva, and for the species B.stellata this is probably the only nesting place in that part of Serbia. In Reserve Zasavica breeding gardener, nesting of the species Phylloscopus trochius, which has not been considered as a breeding ground in Serbia.

Keywords: IBA Zasavica, Birds, 120 years

INTRODUCTION

SNR Zasavica is a unique habitat for birds in northwestern Serbia ie Macva. A specific geographical position on the edge of the Pannonian Basin, near the mouth of the Drina River in the Sava River, as well as various ecological factors enabled the formation and survival of the rich and diverse fauna of birds. The Zasavica basin itself is one of the most important habitats of waterbirds in Macva, such as a breeding ground, a feeding station and a migratory station [1]. Zasavica as a wetland can boast a period of exploration of bird fauna longer than one century. Bird tracking was not continuous, because the data were collected sporadically as a contribution to the entire area's fauna, with major interruptions in research whose breaks sometimes lasted for decades. It is precisely this sporadic research, however, that provides valuable historical data on the bird fauna and habitat conditions that the researchers found. Contemporary data on bird fauna are few in 1995. In the period from 1995. to 1996. year, more intensive research within the framework of the previous protection of the reserve [2] begins. The proclamation of the Zasavica Nature Reserve 1997. [3] and the employment of a research associate establishes the monitoring of complete biodiversity that is still ongoing. In addition to the employed researcher, other ornithologists also visit the reserve, which give their great contribution to the overall knowledge of bird fauna reserves. Because of the great ornithological importance of Zasavica in 2009., declared in the IBA area under the number RS022IBA with a total area of 4670 ha, about 60% of the IBA Zasavica area is located within the Special Nature Reserve and Protection zone. This area has a large number in its borders or less altered natural habitats. For this IBA area, three criteria were identified, from the global IBA category A_1, and from European categories B_1 and B_2 [4]. The aim of this paper is to show the state of the modern Zasavica ornithofauna in relation to historical data.

MATERIAL AND METHODS

All available written data published in the proceedings, professional and scientific papers and reports of ornithological camps, as well as not published data from field journals and oral data were used for writing the work. The research of ornithofauna Zasavica is done with the standard observation methodology through the transect and point, then by marking (ringing) of birds using vertical ornithological networks and others.

RESULTS WITH DISCUSSION

The bird fauna of Zasavica was first mentioned in 1867 by Josif Pancic in the "Birds in Serbia" Book. Even then, Pancic Zasavica is classified into ornithologically important areas for Serbia, where it is said that all herons known in Europe can be seen [5]. The first details and more specific data on the bird fauna of the birds of Zasavica and northern Macva are found in the work of the Austro-Hungarian ornithologist E. Dombrovski [6]. To Serbia 09.09.1893. year. Ernest and Robert Dombrovski, ornithologists, naturalists and preparers, are intending to explore in detail the bird fauna in Serbia, because it was quite well presumed that Serbia's area is extremely rich in bird species due to its belonging to the Central European, South European and Eastern European fauna type.Unfortunately in May, 1894, they leave Serbia for not renewing the work permit and staying in Serbia. The result of these studies is the publication of the Fundamentals of Ornithology of Northwestern Serbia, which lists 203 species of birds, 165 of which are proved by the preparations of individuals and eggs deposited in the collection of the National Museum in Sarajevo [6]. In addition to the data on the fauna of the brothers Dobrovski, they gave valuable and interesting observations about the way of life, behavior and ecology of the species, and the condition of the habitat. The birds that they reliably recorded in Zasavica are: *Podiceps cristatus, Butaurus stellata, Ixobrichus minutus, Nycticorax nycticorax, Ardeola ralloides, Egretta alba, E.garzetta, Ciconia ciconia, Platalea leucorodia, Plegadis falcinellus, Cygnus olor, Anas strepera, A.penelopa, Aythya nyroca, Milvus migrans, Haliaeetus albicilla, Aquila heliaca, Circus aeruginosua, Pandion haliaetus, Falco tinnunculus, Falco vespertinus, Gallinula chloropus, Luscinia svecica, Acrocephalus scirpaceus, A.arudinaceus, Lucustella luscinioides, Panurus biarmicus, Remis pendulinus* and *Emberisa schoeniculus* [6] while the following birds were recorded in the vicinity of Zasavica: *Ardea cinerea, Anas clypeata, Gyps fulvus, Actitis hypoleuca, Recurvirostra avocetta, Larus ridibundus, Chlidonias niger, Asio otus, Strix aluco, Jinx torquilla* and *Acrocephalus schoenobaenus* [7]. By the end of the nineteenth century Đuričić [8] points to the existence of a forest and wetland area in the greater part of the Macva.

By the middle of the XIX century in Zasavica, there were several larger forest beech forest complexes, but they were disembarked in the period from 1860.-1880. years. In the XX century, it continued with devastation and deforestation, but also by mulching the surface, which resulted in the formation of small forest bans, which are usually surrounded by arable land in the modern period. By deforestation most oak forests were the most valuable ones, then the forests of ash and breeds, and at least they were dead or recovered more quickly and restored the forests of willow, poplar and black wolves [7]. During this period, the bird fauna has undergone significant changes, primarily due to anthropogenic activity and drastic changes in the habitat caused by the drying of aquatic habitats, deforestation and reed for increasing the arable land. Many species of birds recorded in Zasavica at the end of the nineteenth century have, in modern times, changed breeding status and are no longer nesting, but are regular or temporary on migration and wandering or on winter. Research in the contemporary period has identified about 30 species that Dombrovski did not record in Macva at the end of the XIX century. Some of the unseen species by Dombrovsky were observed sporadically in the modern period, which indicates that it is possible that they were not accidentally recorded and these are: *Gavia stellata, Bubulcus ibis, Cricaetus gallicus, Falco cherrug, Numenius phaeopus, Tringia erythropus, T.stagnatilis, Motacilla cinerea, Bombycilla garrulus, Turdus torquatus, Sylvia borin,Locustella fluviatilis, Acrocephalus melanopogon, Regulus ignocapillus, Certhia brachydactyla,Hirundo daurica* and *Loxia curvirostra*. Types like are present in the modern period in the Zasavica region, and their nesting or occurrence in the modern period indicates that the boundaries of distribution and changes in the number of populations of these species are displaced [7].

Some of the emaciated nesting hills in Zasavica, such as *Nycticorax nycticorax, Egretta garzetta* and *Ardea cinerea*, are nesting in the vicinity today like a cargo bridge in Sremska Mitrovica and on Zasavica itself, they feed and stay on the seaside. With *Nycticorax nycticorax* and *Egretta garzetta* since 2014., they re-nest in a colony on Sadzak. The former nesting of *Platalea leucorodia* today is regularly seen in the wake and wandering. While some species are rarely recorded in the modern period and mostly as passers-by: *Plegadis falcinellus, Anas strepera, Aquila heliaca, Milvus milvus, Columba oenas, Luscinia svecica* and *Panurus biarmicus*. In the modern period, the finding of the *Columba oenas* after more than a century in Zasavica is significant, in a forest ban at the Salaš Nocajski [9].On Valjevac there are quite dense populations of *Coturnix coturnix, Vanellus vanellus, Motacilla flava, Lanius collurio, Saxicola torquata* and *Miliaria calandra*, which with its 300 hectares represents an important and valuable attention to the open habitat, but also worth conservation efforts carried out by the caregiver. Also on the pasture there are quite thick nests of the *Miliaria calandra* population. Valjevac partly rests on the forests, so that it also plays an important role in the feeding of silvicol species that nest in the forest [7]. Both historical and contemporary data point to large populations of cosmopolitan and eurivalent species such as *Galinulla chloropus, Fulica atra, Acrocephalus arudinaceus* and *Remiz pendulinus* which in Zasavica have very suitable habitats for life and reproduction. Some species such as *Fulica atra* and *Galinulla chloropus* in Zasavica remain throughout the year and in winter. A large number of bird species use the area as a migratory corridor or a wandering area so that the following species of birds can be recorded exclusively in the flyover: *Plegadis falcinellus, Anser albifrona, Cricaetus gallicus, Circus pygargus, Aquila heliaca, A.clanga, Grus grus, Gyps fulvus, Falco vespertinus, Platelea leucorodia, Pandion haliaetus, F.columbarius, F.cherrug, Numenius phaeopus, Larus cachinnans, Sterna hirundo, Apus apus* and *Bombycilla garrulus*. In the forests during seismology and winter, there are wide-spread species with numerous populations in Europe, and many of them are nesting in forests of northern and mountainous areas such as: *Luscinia luscinia, Turdus iliacus, Regulus regulus, Regulus ignicapilus, Ficedula hypoleuca, Fringila montifringilla, Pyrrhula pyrrhula, Carduelis spinus.*

For the separation of the IBA area, 25 species of birds were analyzed, two of which were SPEC 1 (*Aythya nyroca* and *Haliaeetus albicilla*), 4 species are SPEC 2 (*Ciconia ciconia, C.nigra, Vanellus vanellus, Grus grus*) and 8 species are SPEC 3 (*Butaurus stellata, Ixobrichus minutus, Nycticorax nycticorax, Anas querquedula, Milvus migrans, Alcedo atthis, Anthis campestris and Lanius collurio*). According to Puzović *et al*. [4] of 25 species analyzed, 14 species are nesting sites estimated to have number of breeding pairs: *I.minutus* (20-25), *N.nycticorax* (100-140), *C. ciconia* 9-11), *C.nigra* (0-1), *A.querquedula* (6-10), *A. nyroca* (20-25), *P.apivorus* (1), *H.albicilla* (1-2), *C.aeruginosus* (2-3), *F.subbuteo* (3-4), *V. vanellus* (15-20), *A.campestris* (2-3) and *L.collurio* (60-100). In the Zasavica area, six species have the status of SPEC 1, which are: *Phalacrocorax pygmaeus, Aythya nyroca, Haliaeetus albicila, Aquila heliaca, Falco cherrug* and *Gallinago media*, and of these species nesting *A.nyroca* and *H. albicilla* whose number of these species exceeds 1 % of national populations [7,9]. Of the species with the category SPEC 2 as significant nests we distinguish two types of

Ciconia nigra and *Vanellus vanellus*. This category also includes the kind of *Grus grus,* which in large flocks regularly migrates through Zasavica. Among the species with the status of SPEC 3, there are three nesting species: *Ixobrichus minutus, Anas querquedula* and *Coturnix coturnix* [7].

The Mačva has been densely populated for centuries, resulting in an intense and long period of anthropogenic activity. The extremely negative influence of man on the nature of Zasavica is also shown by the major changes in the ornithofaunias that have occurred in the last 120 years, since species like *Anas strepera, Milvus migrans, Aquila heliaca, Falco vespertinus, Panurus biarmicus* and *Luscinia svecica* disappeared as nesting species. Numerous modern studies indicate that Valjevec is one of the most important places in the Macva for migratory species or the feeding and nesting of a large number of rare and endangered species of internationally important species. For some species such as *Vanellus vanellus, Actitis sp*., etc., nesting on the ground, Valjevac is of great importance for their nesting because it is the only large open area in northern Macva with a mosaic distribution of the bar in depressions, wet meadows and step elements on the beams. The Valjevac pasture represents a significant moving station for the type *Grus grus*. Before the sowing of pasture, the flocks are *Sturnus vulgaris, Hirundo rustica, Motacilla flava, M.alba, Ciconia nigra* and others, and the reeds become a significant place for their shelter. So it's 16.09.2012. on Valjevec a group of 55 individuals *Ciconia nigra* and 111 *Ardea cinerea* individuals were recorded. Due to all these values, the preservation of pasture with the remaining fragments of wetlands and steppe elements is one of the priority tasks of the aging person. The mosaic arrangement of moist and dry grass habitats in Valjevac and Jovaca are very important areas for the sowing and feeding of a large number of individuals *Egretta alba, E.garzetta, Ardea cinerea, Ciconia ciconia, Platalea leucorodia, Grus grus, Gallinago gallinago, Tringia glareola, Merops apiaster, Riparia riparia, Turdus pilaris.* Significant changes in the breeding fowl of birds are the result of large ecosystem changes, where the most important is the disappearance of aquatic habitats and shrinkage of reeds and larger complexes of preserved forest surfaces. It is precisely the majority of the missing gorges from Zasavica are species that have great ecological requirements and are closely adapted to life in preserved and food-rich habitats. In the old topographic maps from the beginning of the 20th century, a large marshy complex between Crna bara and Ravnje is visible. At that time, the river Batve at Noćaj and the Glušci was not meliorated, so this part of the Macva represented a separate large swamp. At that time it is estimated that spring flooding was over 25,000 ha, and according to the story of the old villagers, only the pasture Valjevac was under water at a depth of more than one meter every spring. Until the middle of the 20th century, there were floating islands in Zasavica with the *Salix cinerea* and the *Salix alba* trees. The data left by Brothers Dombrovski about the bird fauna and habitat from that period indicate the presence of an extremely important wetland complex in northern Macva, which is no longer present. The main hydro-meliorative works that began in the middle of the 20th century shaped today's appearance of Zasavica. After the Second World War, intensive ameliorative works began, so that between 1950. and 1970. a thick channel network was formed around Bitve, Batar and western Zasavica. In this way, the aquatic habitats around Bitve disappeared, and from the large complex of swamps, only a few canals remained, which were sufficiently eutrophied and grown into reeds and rush. From the former powerful river by which the ships sailed, "Zvornikuše" today Batar is a small, shallow watercourse that has steady water only upstream of the upstream kilometer from the mouth. With the construction of the Modran pumping station in 1964., the water level in Zasavica drastically changed when the large water surfaces disappeared around the watercourse, and the groundwater level decreased considerably. By announcing the Zasavica watercourse for the Special Nature Reserve in 1997., the hydrological image of the terrain is slowly beginning to change for the better. In Zasavica, breeding populations suffered great changes due to the reduction of natural habitats, but besides, IBA Zasavica is an area of national significance for a large number of bird species. For some species of birds, Zasavica is one of the few remaining nesting habitats in northwestern Macva (*B. stellata, C.nigra, A. campestris*). Data on the type *B.stellata* from the period 2007. - 2016. when the singing male singers refer to the nesting of this species in Zasavica and this is probably the only nesting place in that part of Serbia. In IBA Zasavica 215 species of birds are registered, of which 110 species of nesting species are classified into possible, probable and probable breeding nests [10]. According to Atlas, the bird of the Zasavica bird species of 110 species, 80 species (73%) were confirmed, 19 species (17%) are likely and 11 species (10%) are possible breeding reserves [10]. Over 120 years of research on the bird fauna of today's IBA Zasavica area has shown that some species have disappeared and some have settled for the first time. Some of the extinct species, such as *Nycticotax nycticorax, Ardeola ralloides, Ardea cinerea, Egretta alba, E.garzetta*, have begun to re-nest in the reserve since 2014. If in Serbia the total number of nests is 240 species according to Puzović *et al*. [11] then these 110 species in the reserve are 46% of the total diversity of Serbian breeders. The Zasavica Reserve belongs to the region of Macva or Western Serbia, where it is located [11] 163 species of nests were recorded, so that these 110 species in the reserve are 67.4% of the diversity of the gnezdarice of Western Serbia. While working at the Atlas of the Zasavica breeding gardener, nesting of the species *Phylloscopus trochius,* which has not been considered as a breeding ground in Serbia, has been found in the reserve. Comparative analysis of nests in Zasavica and Western Serbia shows that for six species of *Aythya fuligula, Ardeola ralloides, Ardea purpurea, Egretta alba, E.garzetta* and *Ph.pygmeus,* Zasavica is the only breeding ground in Western Serbia. Of the total number of 47 species (43%) there is a stable population, for 13 species (12%) the number has increased, while in 20 species (19%) the number has dropped. In the Atlas of the Zasavica breeders, 110 species were registered in the IBA Zasavica, if the historical data is taken, the number of breeding nets is 120 species. According to the degree of rarity, 47 species of species or 43% are of very rare species (< 25 pairs), 35 species or 32% are rare (25-100 pairs), 14 species or 13% are ordinary species (100-400 pairs) species or 8% are common (400-800 pairs) and 5 species or 4% are very common (800 and 1 pair). Of the many species of nesting people, there are large populations *Oriolus oriolus*, *Luscinia megarhynchos* and *Lanius collurio* or species that are increasingly rare in Europe, and *Galinulla chloropis* is the most common type of aquatic habitats, which is another interesting area of the area.

CONCLUSION

The first data on the fauna of the birds of Zasavica is given by Josif Pančić [5] in the Book "Birds in Serbia", and the first details are given by the brothers Ernest and Robert Dombrovski about the bird fauna of the birds of Zasavica and the whole north Macva, listing 203 species of birds and providing valuable data on behavior, behavior and ecology of species and habitat status. In the period of more than 120 years in the area of today's IBA Zasavica, 215 species of birds were established in the spring of 2018. During this period, bird species have undergone significant changes, primarily due to anthropogenic activity and drastic changes in habitat due to drying and shrinkage to increase arable land.Many species of birds at the end of the nineteenth century have, in modern times, changed nesting status and are now regular or casual on migration and wandering or wintering. Numerous studies indicate that Valjevac is one of the most important places in Macva with a mosaic arrangement of bars, moist meadows and steppe elements on beams for migratory species or feeding and nesting of a large number of rare and endangered species of internationally important species. In the Zasavica area, six species have the status SPEC 1, and in two breeding species (*A.nyroca* and

H.albicilla), the number exceeds 1% of national populations. Most species of nests are related to forest habitats, followed by aquatic and open habitats and the smallest in settlements. Zasavica for some species is one of the few remaining nesting habitats in northwestern Macva, and for the species *B.stellata* this is probably the only nesting place in that part of Serbia.

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DETERMINATION OF SPECIFIC DISCHARGE MODULES OF RIVERS AND CATCHMENT AREAS OF BIG PRESPA LAKE

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Abstract

The aim of this work is devoted to the research for determination the specific discharge module of all rivers existing in various sub-catchment areas which inflow in Big Prespa Lake. Firstly the specific discharge module for each river is calculated on the basis of its average discharge watershed area with tributaries. Then by modeling the value of specific discharge module for each river in all sub-catchment areas which belong to the Big Prespa Lake are calculated. Finally the obtained results from all sub-catchment areas are summarized and tabulated in corresponding already delineated catchment areas of Big Prespa Lake. The determined values of specific discharge modules will serve for future calculation the water budget of Big Prespa Lake.

Keywords: Big Prespa lake, Specific discharge module

INTRODUCTION

Big Prespa Lake is located in the South West of Republic of Macedonia and it is sheared between Republic of Macedonia, Greece and Albania. This Lake is a part of the biggest water system and a unique hydrological ensemble of water in the Balkan Peninsula, formed of three lakes: Ohrid, Big Prespa and Small Prespa Lake. They are the highest tectonic lakes in the Balkan Peninsula and belong to a group of the biggest Desaretic group of the lakes, known as Aegean lake zone [1]. These lakes originate from a geo-tectonic depression in the thercier (Pliocene) period 2 to 3 million years ago on the western Dinarides. Between Big Prespa and Ohrid Lake there is no existing natural surface outflow, but the water from Big Prespa Lake drains by underground links through the Galichica and Mali and Tate mountains and appear as visible surface springs (St. Naum and Tushemishti springs) at the southern coast to Ohrid Lake, which is approximately at 155 m lower attitude than Big Prespa Lake [2-4]. Concerning the Ohrid Lake, the constant level of this lake is regulate by the inflow of ground water mainly from the Big Prespa Lake and surface outflow through the Black Drim River which from Macedonian side cross Albania and inflow in Adriatic sea. The Big and Small Prespa Lakes are located in the deepest part of the Prespa valley at the base of different geological massifs: granite massif of the east, karstic massif on the west and sediments on the north and around the lake shore.

From millions of years the eco-systems Ohrid, Big Prespa and Small Prespa Lakes have coexist in natural harmony, without big pressing of human activities, creating a very beautiful environment with existing rivers, high transparency of pure waters, different flora and fauna and endemic fishes. Prespa is the name of region consisting of two freshwater lakes with the surrounding forests, which extend across the three countries. In 2002 the Prima Ministers of Republic of Macedonia, Greece and Albania jointly declared a new protected area, as the first ecological area in the Balkan Peninsula running across different countries. Today the trans-boundary Prespa Park region is best known for its great biodiversity and its population of rare water birds including the largest breeding colony of the Dalmatian pelicans in the world. This region is also remarkable for its cultural heritage including Byzantines monuments and traditional architecture.

During the last 55 years the hydrological data have shown significant fluctuation of the water level on the Big Prespa Lake [5]. The maximum historical value of water level was recorded during 1963 but in nowadays this level is less than 8 m. In the last 25 years the catastrophic decline of water level of the Big Prespa Lake has been subject to many national and international research projects, but a full scientific explanation for the drop of water level has not been yet fully achieved. The causes have been generally related to phenomena such as: tectonic and geological perturbation of the larger surrounding area, karstic phenomena (change in hydraulic flow conditions of the ground water system or widening of underground channels connecting the Big Prespa and Ohrid Lake), smaller natural fluctuation of rainfall and smaller surface water inflow in the Lake as a result of climate variability. Such variability reflects to the water balance that can result in the change of: precipitation over the lake surface, precipitation over the surrounding watershed, direct evaporation from the lake surface, land surface evapo-transpiration and snowmelt with associated surface runoff and/or groundwater inflow in the lake. But finally it can conclude that the variation and essential decrease of water level is not yet properly explained and more scientific approach to this problem should be consecrated in the future.

The aim of this study is consecrated to determine one of the key parameters as specific discharge modules of rivers and catchment areas of Big Prespa Lake, for calculation of water balance and try to estimate which of above mentioned parameters has a bigger influence to the water level declination.

MATERIALS AND METHODS

For realization the aim of this study, various methodologies have been used depending of hydro-meteorological techniques installed in various location around the Big Prespa Lake shore and Prespa valley, as well as mathematical analysis of measured data, calculation of some hydro-meteorological parameters and theirs interpretation. For valuable determination of any key parameters as; specific discharge modules of rivers and catchment areas of Big Prespa Lake, it is necessary continuous performed the measurement more than 10 years, or best about 30 years. Then the average calculated value should be used for estimation the long term fluctuation and change in water budget as the indicator for the main causes of water level declination. For the long time the data have been generally red manually from old hydro-meteorological techniques. Recently, in some hydro-meteorological stations these old techniques have been replaced with new ones where the measured data are recorded continuously and automatically. For determination of specific discharge modules of inflow rivers the water level of these rivers has been measured with classical non-recording graduated vertical staff gauges. In last decade some new recording gauge have been installed in some places but only of bigger rivers. The water discharge of permanent streams and occasional appearance of streams during the rains and storms are estimated through the other long time measurements. Discharge at a given time can be measured by several different methods and the choice of the method depends on the conditions encountered at a particular side.

In the case of the Big Prespa catchments area the discharge of the rivers and some bigger streams are performed by current meters. The discharge is expressed as a volume of water per unit time, which flows through a cross-section. The depth of flow in the cross section is measured at verticals with a graduated rod and the velocity of flows is obtained with a current meter at more points in the verticals fig.1. The measured widths, depths and velocities permit computation of discharge for each segment of the cross section [6]. The summation of these segments discharges is the total discharge. Discharge measurements need to be made at the previously selected exact locations of the stage gauges because the discharge is normally the same throughout the reach of channel in the general vicinity of the gauges. Site selected for measurements should have the following characteristics: (a) the velocities at all points are parallel to one another and at right angles to the cross section of the stream, (b) the curves of distribution of velocity in the section are regular in the vertical an horizontal planes, (c) the velocity is greater than 0.15 m/s, (d) the bed of the channel is regular and stable, (e) the depth of the flow is greater than 0.3 m, (f) there is no aquatic growth, (g) there is minimal formation of slush or frazil ice.

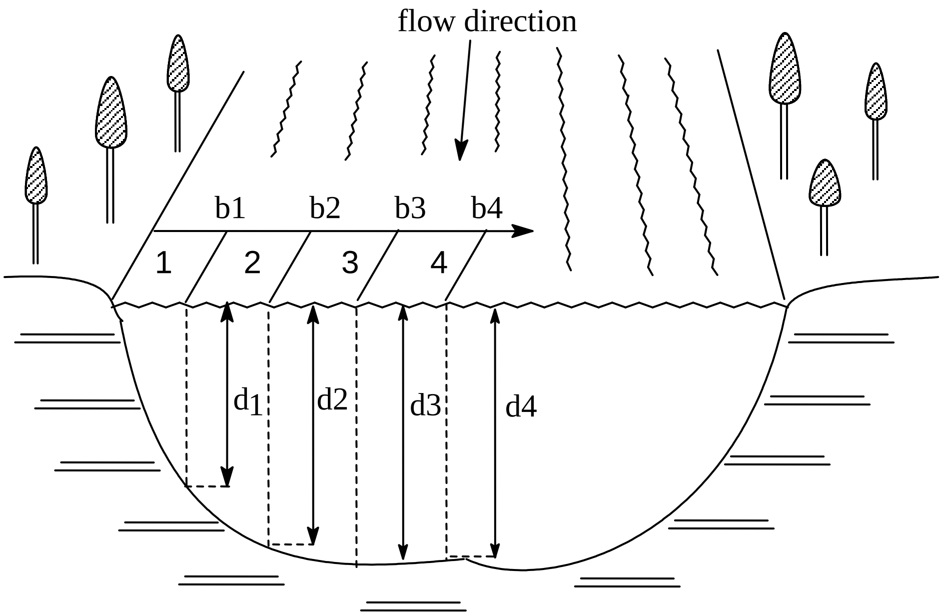

Figure 1 *View of river cross-section showing the location of measurements point*

The accuracy of a discharge measurement depends on the number of verticals at which observations of depth and velocity are obtained. Observation points of verticals should be located so to best define the variation in elevation of the stream bed and horizontal variation in velocity.

The velocity of flow at a point is usually measured by counting rotations of a current meter rotor during a short-time period measured with a stop watch. Velocity is observed at more points during a period of not less than 60 s and not more than three minutes, if velocities are pulsating. After the meter has been placed at the selected point in the vertical, it should be allowed to become aligned with the direction of flow before readings are started.

The total discharge is obtained by adding the discharge from each segment. The discharge in each section is computed by multiplying velocity and depth $v_i\, d_i$ in each vertical by a width which is the sum of half the distance to adjacent verticals. The value of *d* in the two half widths next to the banks can be estimated. The total discharge *Q* is computed as:

$$Q = v_1 \cdot d_1 \cdot \left(\frac{b_2 - b_1}{2} \right) + v_2 \cdot d_2 \cdot \left(\frac{b_3 - b_2}{2} \right) + ..v_i \cdot d_i \left(\frac{b_{(i+1)} - b_i}{2} \right) \quad (1)$$

RESULTS AND DISCUSSION

The Big Prespa Lake is supplied with waters from underwater resources and several rivers and streams that flow into the lake from Macedonian, Greek and Albanian side. But the main recipient of all waters that flow through the Prespa valley and inflow to the Big Prespa Lake are the rivers: Golema Reka, Pretorska Reka, Kranska Reka, Kurbinovska Reka, Istocka Reka and Brajcinska Reka on Macedonian side, as well as Agios Germanos on Greek side.

The catchments areas of Big Prespa Lake have been delineated on the basis of topographic maps of Republic of Macedonia and under consultation of digital LANDSET satellite images of August 2000 which have been integrated into a Geographic Information System (GIS). Prespa Lake watershed was divided in 4 hydrological catchments areas for the purpose of rainfall-runoff modelling. Each of these four areas, named: East, South, West and North, has different properties, as a consequence of various: exposure, geology, slope, land cover, land use and surface outflow. The other reason is use of the available meteorological and hydrological data and grouping of the small sub-catchments areas with similar properties into larger hydrological units.

The specific discharge modules of catchments areas can be determined from the specific discharge module of the rivers existing on the observed catchments areas.

For each river the specific discharge module can be calculated with the equation:

$$q = \frac{Q_{RR}}{A_{wR}} (l/s/km^2) \quad (2)$$

Q_{RR} – average discharge, or run-off of observed river *(l/s)*

A_{wR} – watershed area of the observed river (km^2)

However, it should be mentioned that for each observed river, *q* is not a constant value and generally it changes along the river length. This module also varied depending on the rain-fall over the watershed area because for more intensive rain-fall the run-off is bigger.

The watershed areas of some rivers on the Macedonian side are delineated in consultancy with the hydro-meteorological Institute in Skopje [7,8],

For example, in the North part of the Big Prespa Lake the watershed area of Golema River with its tributary up to the measuring gauge in Resen city is 93.99 km^2. The average discharge of Golema River in Resen in the period of last 30 years is Q_{RR} = 0.887 m^3/s. By equation (2) the specific discharge module of this river can be calculated:

$$q = \frac{887}{93.99} = 9.44 (l/s/km^2) \quad (3)$$

Using the specific discharge module for all existing rivers, calculated on the basis of their average discharge watershed area and tributaries in various sub-catchments areas by modelling, the value of the specific discharge module for each of the sub-catchments areas is determined according to equation:

$$q_{AV} = \frac{Q_{RAV}}{A_C} (l/s/km^2) \tag{4}$$

q_{AV} – average specific discharge coefficient of observed catchment area

Q_{RAV} – average run-off from observed catchment area (l/s)

A_C – catchment area (km^2)

In Table 1, the result for the modelling determined from the data from the hydro-meteorological institute in Skopje (average 30 last years) is given.

Table 1 *The result of modelling from data of hydro-meteorological institute in Skopje*

Name of sub-catchments	Sub-catchment area (km^2)	Average Q (m^3/s) Run-off	Annual Q MCM/annual	Specific discharge module (l/s/km^2)
North	405	5.10	161	12.59
East	246	3.18	100.3	12.92
West	181	0.49	15.4	2.70
South	225	2.08	65.7	9.2
	Sum 1057	Sum 10.85	Sum 342.4	Aver 10.27

As it can see from Table 1, the difference of total annual run-off is noticeable, mainly as a result of big difference of run-off in the western catchment area. Taking into account that in the west catchment area there is no surface rivers (only apparition temporary streams during the storms) and that the geomorphology of the terrain is karstic (limestone), it seems that run-off in the western by modelling should be difficult to find the reliable value with small displacement.

CONCLUSION

The determined value for specific discharge modules of rivers and catchments areas are calculated on the basis of hydro-meteorological and geological data obtained from respective institutions from all three neighbouring countries: Macedonia, Greece and Albania. The delineation of catchments and sub-catchments areas are enough compatible while small difference exists in some meteorological parameters especially in precipitation over the lake surface and for quantity of evaporation from open lake surface. But these differences do not influenced noticeable in determination of specific discharge modules, so we strongly believe that the obtained results are in big measure valuable and will serve in future calculation the water budget of Big Prespa Lake.

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PESTICIDES AND THE LOSS OF BIODIVERSITY: EUROPEAN HARE

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Abstract

Over the past 40 years, the use of highly toxic pesticides has strongly increased, especially in Serbia as a country with a long agricultural tradition. The European hare poisoning depends on pesticides' toxicity and other properties (the quantity applied, frequency, timing and the method of spraying, the weather, the vegetation structure, and the soil type). The wildlife is exposed to insecticides, fungicides and more toxic herbicides. With the habitat changes, pesticide poisoning can cause major population decline which may threaten rare species. The liquid chromatography - tandem mass spectrometry technique combined with the electrospray ionization, LC–MS/MS(ESI), was applied for the detection of 96 pesticides in European hare adipose tissue collected during 2016. The samples of the European hare adipose tissue were collected from 6 localities in Vojvodina. The individuals of the European hares were up to one year old and belonged to the third age group. The applied one-way ANOVA analyses showed statistical significances among different localities (p_m=0.024259 for $p<0.05$) but not for pesticide concentrations (p_p=0.197812 for $p<0.05$). The post hoc Fisher's LSD test highlighted Bačka Palanka as the locality with the highest concentrations of the observed pesticides in the European hare adipose tissue.

Keywords: European hare, Pesticide residues, LC-MS/MS

INTRODUCTION

The earth's biodiversity is currently being lost at an alarming rate. Changes in habitat and biodiversity are being caused by the changing climate and people's increasing use of plant and animal resources [1]. Arable and pastoral farmlands are the dominant land use in Europe, accounting for over 47%. With an estimated 50% of all European species reliant on agricultural habitats, it is perhaps no surprise that some critical conservation issues relate to changes in farming practices and the direct effect this has on the wildlife on farms and adjacent habitats [2].

The agricultural intensification, the use of pesticides, especially insecticides and fungicides, have had the most consistently negative effects on species diversity. The UK Food and Environment Research Agency indicates that between 1990 and 2006 the total area treated with pesticides increased by 30% in the UK and that the herbicide-treated area increased by 38% [3]. The very same situation is in the countries with a long agricultural tradition as Serbia. The agricultural impact could lead to habitat loss and environmental damage due to pesticides being dispersed into the environment [4]. By the dramatic increase in the areas under the agricultural crops in Serbia with the intensive use of pesticides and the decrease in areas under fodder crops the possibility of qualitative nutrition for hares is decreased parallel with the change of their typical habitats [5,6]. Hares feed on grass, weeds, various agricultural crops, vegetable plants, buds, fresh trees bark and grains. They provide the sufficient amount of water through succulent plants so that they almost need no water [7].

That is why the aim of our study was to determine the pesticide residues in European hare adipose tissue and made the statistical analyses of pesticides influence on loss of biodiversity.

MATERIALS AND METHODS

Chemicals and aparature

The analitical pesticide standards were manufactured by Dr. Ehrenstorfer GmbH, Germany. As an internal standard (IS) carbofuran-D3 (99.7%, 10.0 μg/mL) was purchased from Pestanal, Fluka (Germany). The stock standard solutions were prepared in MeCN while the. the mixture of the studied pesticides was obtained by mixing and diluting the stock standards with MeCN resulting in the final mass concentration of 10.0 μg/mL.

For LC analysis, an Agilent 1200 (Agilent Technologies, USA) HPLC system was used. LC was equipped with a reversed-phase C18 analytical column of 50×4.6mm and 1.8 μm particle size (Agilent Zorbax Eclipse XDB). The mobile phase was methanol and Milli-Q water with 0.1% formic acid in gradient mode, with the flow rate 0.4 mL/min. For the mass spectrometric analysis, an Agilent 6410 Triple-Quad LC/MS system was applied. Agilent Mass Hunter Data Acquisition, Qualitative Analysis and Quantitative Analysis software were used for method development and data acquisition.

Validation

Within the validation the recoveries of extraction, detection limits (LOD), quantification limits (LOQ) and linearity with IS were determined according to SANTE/11813/2017 [8]. The LOQ was established concerning MRLs [9]. The LOD was calculated by MassHunter Qualitative Software. The linearity was checked using matrix matched calibration at the concentrations of 5.0, 10.0, 25.0, 50.0 and 100 ng/mL. The recovery was checked for three fortification levels 0.10, 0.05 and 0.01 mg/kg.

Sample preparation

The European hare were collected from the agricultural areas from Vojvodina region, from Brestač, Bačka Palanka, Bešenovo, Čantavir, Sonta and Stejanovci location. The fatty tissue samples were immediately collected and put in dark plastic bags and kept in the freezer until they were analyzed.

QuEChERS extraction

10 g sample + 10 mL MeCN + 100 μL - Shake vigorously for 1 min
Add 4 g $MgSO_4$, 1 g NaCl, 1 g Na_3Citrate dihydrate, 0.5 g Na_2HCitrat sesquihydrate Shake tube immediately for 1 min - Centrifuge for 5 min at 4000 g
Transfer 6 mL of the extract into a PP tube contained $MgSO_4$, PSA, C18 Shake for 60 s - Centrifuge for 5 min at 4000 g
Transfer into a vial → LC-MS/MS

Statistical analyses

In order to obtain statistical results, the factorial and one-way analysis of variance (ANOVA) were performed following by Fisher's LSD post hoc test. (Dell™ Statistica™ 13.2, University licence).

RESULTS AND DISCUSSION

The factorial ANOVA did not show any statistical significances regarding the influence of the paired values of different localities and pesticide concentrations (p_{lxp}=0.556871 for $p<0.05$) as independent variables on the pesticide residues as the dependent variables, the same as one-way ANOVA calculated for different pesticide concentrations (p_p=0.197812 for $p<0.05$) (Figure 1). However, the applied statistical analyses emphasized statistical significances among different localities (p_l=0.024259 for $p<0.05$) as independent variables (Figure 2), where the Fisher's LSD test accentuated Bačka Palanka as the locality with the highest concentrations of observed pesticide residues in the European hares.

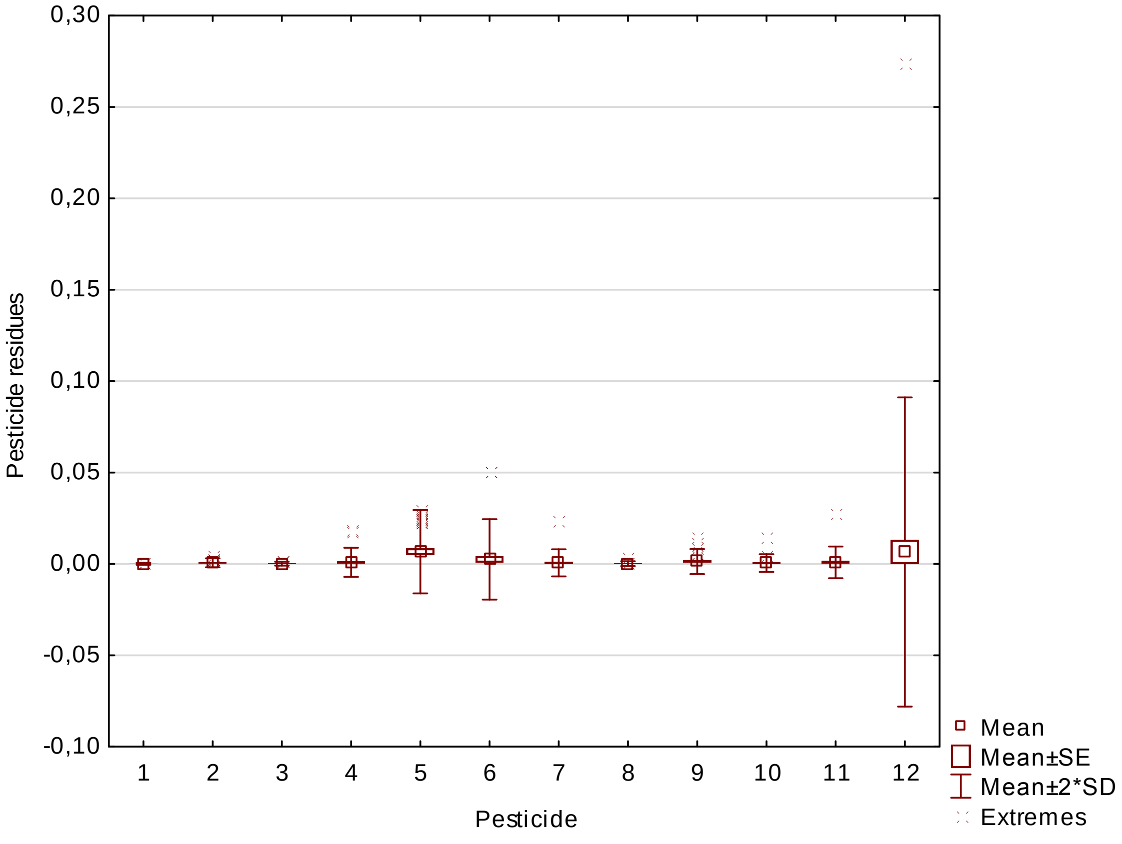

Figure 1 *Box plot calculated for different pesticide and pesticide residues (1- Azoxystrobin, 2- Carbendazim, 3- Chlorphyrifos, 4- Cyproconazole, 5- Cyprodinil, 6- Difenconazol, 7- Pirimifos-methyl, 8- Propoxur, 9- Pyrimethanil, 10- Tebuconazol, 11- Thiamethoxam, 12- Trifloxystrobin)*

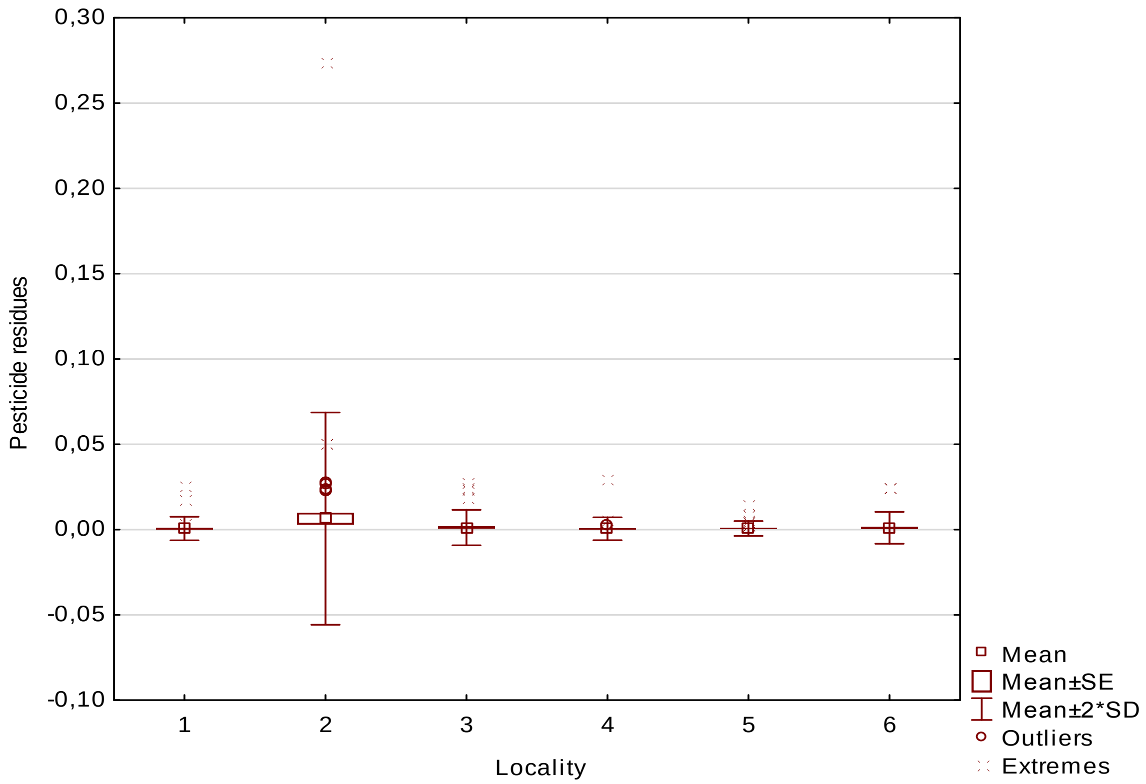

Figure 2 *Box plot calculated for different localities and pesticide residues (1- Brestač, 2- Bačka Palanka, 3- Bešenovo, 4- Čantavir, 5- Sonta, 6- Stejanovci)*

CONCLUSION

The applied statistical analyses depending on the pesticide residues in the European hare fatty tissue and the localities Brestač, Bačka Palanka, Bešenovo, Čantavir, Sonta and Stejanovci emphasized the statistical significances among different localities. Bačka Palanka is the locality with the highest concentrations of the observed pesticide residues in the European hare and could be the crucial reason for the loss of biodiversity.

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GRASSLANDS IN ECOREMEDIATION IN AGRICULTURE, URBAN ECOSYSTEMS AND LANDFILLS

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Abstract

Today, more and more undesirable areas are being made into the grasslands, places like landfills could become places of recreation and gathering centers with enough knowledge. For the establishment and care of lawns, a lot of professional knowledge is required as well as practical experience. The diversity and intensity of the applied care measures depend on the type of grassland, which can be park, decorative and highly decorative lawns, then sports fields (football fields and golf courses). One of the latest innovations in the world is artificial synthetic lawns that are used in places where natural ones cannot survive. Such solution is not inherent in sustainable development, and therefore in inaccessible places, the best choice of different plant species should cover even the most decent degraded land. A properly raised lawn is only one part of a job well-done, as further maintenance of the green surface is equally important. On these grasslands, the most productive family species of the fam. Poaceae and fam. Fabaceae are predominant. For the planting of grassland, varieties of ryegrass (Lolium perenne), common meadow-grass (Poa pratensis L.), meadow fescue (Festuca sp.), cocksfoot (Dactylis glomerata L.) and meadow cat's-tail (Phleum pratense) are most often used. In general, any investment in green areas is profitable because it creates attractive places for domestic and foreign tourists from various countries, which supports tourism from which the community can benefit even more.

Keywords: Urban green infrastructure, Landfills, Sustainable development, Lawns

INTRODUCTION

Despite the great advancement of science and technology, many negative changes in soil occur, and they are even greater if more advanced land-processing technology, and therefore the living standard of people and a more intensive process of urbanization and industrialization.

Considering that a man uses resources from the soil for his life and work, everything that endangers the land, endangers his health and survival [1]. Lawns, as surface areas covered by annual, biannual and perennial herbaceous plants today, cover large areas and represent one of the most important biosphere factors [2].

The grassland plant communities are well adapted to different agro-ecological and soil conditions. In the most favorable areas of moderate humid climate and on the lands of more favorable chemical and physical properties communities are formed which are called valley meadows. On these grasslands, the most productive family species of grasses (fam. Poaceae) and legume (fam. Fabaceae) are predominant. In the mountainous regions, communities are formed with species that are adapted to less favorable agroecological and soil conditions [3]. With an increase in altitudes, altered environmental and soil conditions have influenced the formation of lawns in which the most represented species are better adapted to these areas, but also have smaller productive qualities [4].

The importance of the grasslands for man is seen in two aspects. Since the beginning of human history, grasslands provide the opportunity to provide feed during the whole vegetation season. In recent times, the secondary role of grasslands is used to revegetation of public areas and infield, then for sports fields, to protect against erosion on the slopes along the roads and riverbeds. Over the past several decades, in some developed countries, attempts have been made to produce biomass on the natural grassland in accordance with the principle of "sustainability", according to [5]. This agrotechnical system implies the achievement of higher yields and quality of fodder, with a reduction in investment in production, as well as the preservation of biodiversity in grasslands and the environment in general [6].

Grassland plants play an important role in an overall agricultural production. With their presence, this plant significantly stabilizes the soil, prevents erosion, the introduction of chemical preparations into the soil, which would rinse into groundwater by leaching. Legumes on pastures, with the help of symbiotic nitrogen-fixing bacteria, synthesize significant amounts of nitrogen compounds and thus reduce the costs of enhanced mineral nutrition of plants. By their presence, nitrogen bacteria increase the fertility of the soil directly by increasing the quality of animal feed.

Sown pastures, in relation to natural, have a number of advantages and have gained an increasing importance in the past decades. If they are used for agricultural purposes, these grasslands give higher annual yield and quality of biomass, because better production results can be achieved by correct selection of species in the mixture [2]. Intensive agro-technical measures are applied in the lawns, which also contributes to the increased volume of animal feed production.

Pollution influenced by anthropogenic activities (industrial, intensive agriculture, traffic, municipal and hazardous waste disposal) disables the production of health-safe food on significant land surfaces, and intensively develops bio-based methods for its remediation. Grassland plants in this process can be used in an environmentally and economically sustainable way [7].

The aim of these investigations is to provide a brief overview of the importance of lawns in agriculture, environmental protection and urban ecosystems.

RESULTS AND DISCUSSION

Types of grass suitable for pasture establishment

For the establishment of lawns used for agricultural purposes, it is necessary to sow the most productive types of grass, and the varieties that give quality biomass [8]. For grass surfaces of special purpose, grasses of pleasant appearance are selected, which are well-groomed and grass carpets are formed and are tolerant of wade. For such grassland, it is necessary to take into account the biological characteristics of the species, subspecies, or variety, the conditions of the external environment and the soil, as well as the locality that will be established.

A large number of predominantly perennials are nowadays harvested thanks to the work of breeders who have created a series of genotypes for different purposes. For the planting of lawns, the most commonly ryegrass (*Lolium perenne*), common meadow-grass (*Poa pratensis* L.), meadow fescue (*Festuca* sp.), cocksfoot (*Dactylis glomerata* L.) and meadow cat's-tail (*Phleum pratense*) cultivars were used [9,10].

Ryegrasses are a very important group of meadow species that appear on a large geographical area, from moderately humid, to the drier areas of Asia, Europe, to America. Thanks to the high potential of fertility and biomass quality, some species have been cultivated back in the 13th century and are used and used in many ways (meadows, pastures, lawns for special purposes). The greatest economic significance is due to *Lolium multiflorum* L., *Lolium perenne* and *Arrhenatherum elatius* [9].

Poa pratensis and other species belonging to Poaceae are present in sown meadows and pastures. Species from genus *Festuca* represent a very important group of meadow-pasture species that occur on natural and lawn grasslands.

Dactylis glomerata is growing increasingly in sown meadows and mixed with alfalfa (*Medicago sativa*) and other legumes. There are many varieties of *Dactylis glomerata* that are being prepared for the production of hay, also in fresh condition and used in the feeding. It can also be cultivated as a feed for annual planting plants, for example in the cattle grain pond as a cover crop that provides a firm support to the basic crop. High yield and significant nutritional value of biomass, if the cuts are previously classified as a ridge in the group of the most important cultivated grasses in natural and lawn grasslands. It is used on sow grasslands for 5-6 years, and the maximum production of biomass is from the second year. Although it is mainly cultivated in meadows, there are varieties that are subjected to bumping so they can be sown in mixtures with pasture species.

The *Phleum pratense* is one of the most important grasses grown on meadows, most often as pure crops. It regenerates well and gives 2-3 rows in the season. Biomass is an excellent cereal food that is used fresh or as a hay. Plants do not tolerate long-term patches, so it is rarely used for silage. This species is suitable for cultivation with the application of high agro-technology.

Table 1 *Mixtures for regeneration of degraded grasslands in protected areas [11]*

First mixture	Second mixture
Festuca pseudovina, 67%	*Festuca rupikola*, 40%
Poa angustifolia, 33%	*Bromus inermis*, 30%

Grassland restoration in former arable lands offers a great opportunity to mitigate the overall loss of grassland biodiversity with another benefit in weed control especially in abandoned croplands [11]. The plant mixtures are recommended for protected areas (Table 1) and degraded soil on roadside or waste dumps (Table 2) due to rapidly forming cover of sown grasses effectively suppressed short-lived weeds and their germination except in the first year.

Table 2 *Mixtures for grasslands near road and waste dumps [11]*

Plant species	Share	Plant species	Share
Festuca rubra L.	35%	*Festuca rubra* L.	50%
Lolium perene L.	25%	*Poa pratensis* L.	20%
Poa pratensis L.	25%	*Trifolium repens* L.	15%
Lotus corniculatus L.	15%	*Agrostis alba* L.	15%

The impact of grasslands on the city landscape

Grasslands play a major role in urban areas when it comes to lawns for special purposes. Grasslands on the city surfaces connect a man with nature, lower the temperature during the summer, have a sports-recreational character an irreducible value. In general, the grass surfaces influence the agroecological conditions of the environment, which becomes more fresh and healthier. Lakic *et al*. [12] point out that the diversity and intensity of the applied care measures depend on the type of grassland, which can be park, decorative and highly decorative lawns, then sports fields (football fields and golf courses). It should be noted that for the construction and maintenance of sports fields, investments are intensive because they are very demanding lawns. The main purpose of the counterweight lawns is protective so that there are prevailing species that their great roots bind soil and prevent erosion [13].

Grasslands help purify polluted air and oxygen extinguishing so that these areas better preserve a healthy environment and maintain a biodiversity. The influence of the lawns on the heat regime is favorable because they can lower summer air temperatures by 2-3 °C [2]. Lawns improve the surface layer of the soil by absorbing large amounts of different inorganic compounds (carbon dioxide, salts and the like) and thus favorably affect the physical, chemical, and biological properties.

Depending how much is invested in the formation of such surfaces depends on the economic situation. Developed countries (Netherlands, Germany, Switzerland) have decorated green surfaces that serve as an example. Adding to this is the fact that the culture of nature conservation in cities needs to be developed daily and that education is done on the population, as well as the introduction of legal penalties when such areas are endangered.

Any disregard for the nature of those who created it themselves or those created by man, in order to make the living conditions better, should be strictly sanctioned. Unfortunately, such measures are still not implemented, although there is a basis for their implementation in the near future. In general, any investment in green areas is profitable because it creates attractive places to visit domestic and foreign tourists from various countries, which supports tourism from which the state can benefit even more.

Lawns are common in strict urban areas, such as squares. Skilled experts in the field of horticulture can make a true portrait, which in time becomes worthy of admiration in the developed cities that organize various seminars, tourist manifestations, exhibitions. Generally, such artistic creations eventually emerge from the engineering framework, and by combining skills and creativity they become artistic works, and rightly it can be said that the founding of decorative lawns is the same as the science and art of [6].

Grassland plants in ecoremediation

Remediation of soil contaminated with organic or inorganic pollution is a method of the first choice because it is significantly cheaper than physical and chemical methods that can be used for the same purposes and at the same time environment-friendly [14]. Polycyclic aromatic hydrocarbons (PAHs) are of considerable concern because they are potentially toxic to humans and are persistent contaminants in the environment. Phytoremediation, the use of plants to remediate contaminated soil, has been described as a promising approach to remediate soils contaminated with persistent organic pollutants such as PAHs. During the last few decades, found many plant species including alfalfa and tall fescue to be promising candidates for phytoremediation of PAHs [15]. Of inorganic pollution are the most important heavy metals that can also be removed or immobilized using grassland plants in the process of phytoremediation [7]. Significant results were achieved by the use of Fescues in Pb absorption [16]. Grassland plants have been successfully used for the capping of municipal waste landfills after closure (Fescues, Alfalfa) and have also been applied in land remediation degraded by mining activities and electricity production in thermal power plants (Table 3) [17].

***Table 3** Mixtures for the biological reclamation disposal of ash and slag from TPP [17]*

Grass	Share	Legume	Share
Festuca rubra L.	20%	*Lotus corniculatus* L.	15%
Poa pratensis L.	20%	*Trifolium pratense* L.	10%
Phleum pratense L.	20%	*Medicago sativa* L.	10%
Dactylis glomerata L.	20%	*Pisum sativum ssp. arvense* L.	5%

Recultivated surfaces are used primarily for recreation and tourism, thus re-valorizing their values. Large investments are needed for the establishment and maintenance of sports fields. The main purpose of the counterweight lawns is protective so that there are prevalent species in the soil that perfectly bind the soil and thus prevent erosion. In general, any investment in green areas is profitable because it creates attractive places to visit domestic and foreign tourists from various countries, which supports tourism from which the state can benefit even more.

CONCLUSION

Natural and sown grasslands show significant effects in the sustainable development of agriculture, urban systems, and degraded land, primarily from the environmental aspect.

- In agriculture: for the production of food for domestic animals while preserving and improving soil quality,

- there are many varieties of specific morphological features in the world that are intended for green areas for various sports (for football fields, for golf courses, for tennis courts and so on), while on luxurious decorative lawns of landscapes and urban areas there are varieties grass that has decorative leaves in different shades of color.

- more and more undesirable areas such as landfills are being closed and, with enough knowledge, they become places of recreation and gathering centers. For the establishment and care of lawns, a lot of professional knowledge is required as well as practical experience.

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STANDARDS IN MANAGING OF THE CHEMICALS

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Abstract

Standard - a document defines rules, guidelines, or characteristics for activities or their results (a product or service may be the result) in order to achieve an optimal level of regulation. Standards largely have a positive impact on most aspects of our lives. They provide desired characteristics of products and services such as quality, positive environmental performance, safety, reliability, efficiency and interchangeability. When products and services are in line with our expectations, we take it for granted and do not even know the role of the standard. However, if the standards do not exist, we would very quickly notice this. We would be bothered by the fact that the products are with bad quality, which are not appropriate, incompatible with the equipment we already own, or are unreliable and dangerous. When products, systems, machines and appliances work well and safely, this is mainly because they feel out the requirements of the standard. How do standards help us? make development, production and distribution of products more efficient, safer and cleaner; harmonize trade between countries; enable exchange of technology and good management practices; expand/spread innovation; provide customers and users of products and services; make life easier by finding out solutions to everyday problems.

Keywords: Standard, Positive environmental performance, Quality

INTRODUCTION

The most important feature of the standard, which distinguishes it from regulations, norms or laws, is that it is NOT MANDATORY. At the moment when its mandatory application by state institutions is prescribed, it goes from the standard to a technical regulation or norm.

Standardization or introduction of standards into a system has the main goal of helping to solve problems in functioning of work processes and ensuring that the product or service that comes out of the process is of adequate quality for the end user.

Through the management of chemicals, we encounter various rules and standards.

For the registration of chemicals, classification, packaging, labeling, standards are used to determine certain properties of substances or mixtures, so that they can be properly classified, packaged, labeled, in order to be handled correctly and placed, as such, on the Serbian market.

DISCUSSION

Law on Chemicals:

Part of definition of the term Cleansing refers to the standard SRPS ISO 862: 1994 - Surface active substances - Vocabulary

Classification is performed pursuant to the criteria for classification and labeling of substances and mixtures

During the classification, the rules, ie criteria and standards must be complied with!

There is a procedure-criterion in the classification rulebook.

Flammable gases

Flammability of gases and mixture of gases is determined by methods of testing or, in case of mixtures for which there is sufficient data, by calculation methods in accordance with SRPS ISO 10156 ("Gases and gas mixtures - Determination of ignition and oxidation ability in the selection of discharge valves for bottles").

When there is not enough data available, a test method can be used in accordance with SRPS ISO 1839 ("Determination of explosion limits for gases and vapors").

Flammable aerosols

The chemical heat of combustion can be found in literature, calculated or determined based on the test (see standard SR PS B.H8.153 - "Standard method for determination of heat of combustion of liquid hydrocarbon fuels using a calorimetric bomb", standard SR PS EN ISO 13943, 86.1 to 86.3 - Fire safety - Vocabulary and Guidelines for the production and storage of aerosol products - NFR A 30B).

Oxidising gases

Method SRPS ISO 10156 or SR PS ISO 10156-2

In order to classify a gas or mixture of gases in the class of oxidizing gases, tests or methods of calculation are used, as explained in SRPS ISO 10156 ("Gases and mixtures of gases - Determination of ignition and oxidative ability in the selection of discharge valves for bottles"), for gas cylinders in SRPS ISO 10156-2 ("Gas cylinders - Gases and gas mixtures - Part 2: Determination of oxidation ability of toxic and corrosive gases and mixtures of gases”).

Standards used in the classification of flammable liquids

SR PS EN ISO 1516: 2010 - Determination of "inflammable / non-flammable" method - Balance method in a closed container

SR PS EN ISO 1523: 2008 - Determination of the ignition point - Balance method in a closed container

SR PS EN ISO 2719: 2008 - Determination of the ignition point - Pensky-Martens closed container method

SR PS EN ISO 3679: 2008 - Determination of the ignition point - Rapid balance method in a closed container

SR PS EN ISO 3680: 2010 - Determination of "flammable / non-flammable" – Rapid balance method in a closed container

SR PS EN ISO 13736: 2014 Determination of the ignition point - Method in a closed container according to Abel

SR PS B.H8.047: 2012 - Testing of mineral oils and other flammable liquids - Determination of the ignition point in a closed container according to Abel-Pensky

SR PS EN ISO 3924: 2012- Petroleum products - Determination of the boiling range - Gas chromatography method.

Substances and mixtures corrosive to metals. A substance or mixture that causes metal corrosion is a substance or mixture that can damage or even destroy metals by a chemical reaction - SRPS ISO 3574: 2014- Cold-rolled carbon steel sheet for general purpose and deep drawing.

The Regulation on Classification, Packaging and Labeling has certain deviations

With portable gas cylinders with a capacity of up to 150 liters, one of the deviations can be used:

1) Shape and dimensions in line with SR PS ISO 7225: 2010 + EN ISO 7225: 2010 / A1: 2013 - Gas cylinders - Warning labels (in this case, a label may be a generic, industrial or trade name of a substance or mixture if hazardous substances are listed on the cylinder itself in a clear and recognizable way.

2) The labeling elements referred to in Article 18 of this Regulation may be found on a permanent information disc or on a label printed on the cylinder itself.

Gas containers intended for the storage of propane, butane or liquefied petroleum gas (TNG)

If propane, butane and liquefied petroleum gas or mixtures containing these substances classified according to the criteria given in this annex are placed on the market in closed reusable bottles or in disposable single use containers in accordance with SR SR EN 417 Metallic single-use bottles for liquid gas, with or without a valve, intended for portable appliances - Design, control, testing and labeling as fuel used only as combustion gases, then such bottles or containers are labeled with appropriate pictograms and hazard warnings and information on precautionary measures related to flammability.

Special rules for additional labeling elements for certain mixtures

Lead containing mixtures

SRPS ISO 6503:2010- Paints and varnishes - Determination of total lead - Flame atomic absorption spectrometric method

Special rules for packaging

Packaging containing a substance or mixture intended for general use and classified according to acute toxicity, category 1, 2 or 3, specific target organ toxicity - single exposure, category 1, specific target organ toxicity - multiple exposure, category 1, or as corrosive to skin, category 1, has a cover that makes it difficult for children to open.

Packaging containing a substance or mixture intended for general use poses a risk of aspiration and is classified and labeled in accordance with the regulations, with an exception of substances and mixtures which are placed on the market in the form of aerosols or in containers equipped with a sealed spray, has a cover that makes it difficult for children to open.

Additionally, if it contains methanol more than 3% or dichloromethane more than 1%, it has a cover that makes it difficult for children to open.

SRPS EN ISO 8317:2009- Packaging is safe for children - Requirements and test methods for packaging intended for multiple opening.

SRPS EN 862:2010- Packaging - Packaging safe for children - Requirements and test methods for disposable packaging intended for non-pharmaceutical products

Fulfillment of these conditions can be established in laboratories with SRPS ISO / IEC 17025: 2006- General requirements for the competence of testing laboratories and the calibration laboratory

A tactile warning

SR PS ISO 11683:2005- Packaging - Tactile warning symbols for danger - Requirements

Packaging of a substance or mixture intended for general use and classified in relation to: acute toxicity; corrosive skin damage; germ cell mutagenicity, cat. 2; carcinogenicity, category 2; reproductive toxicity, category 2; sensitization of respiratory organs; specific target organ toxicity, category 1 or 2; danger of aspiration; or classified as flammable gases, liquids and solids or mixtures, categories 1 or 2, contains a tactile hazard warning.

Except for aerosol-flammable category 2 and portable gas cylinders

Restrictions and prohibitions - Rules on restrictions and prohibitions are regulated:

Restrictions and prohibitions of production, placing on the market and use of certain substances, mixtures and products

Restrictions and Prohibitions of Persistent Organic Pollutants (POPs)

Restrictions on the total content of volatile organic compounds (VOCs) in certain paints, varnishes and vehicle repair coatings

Regulation on restrictions and prohibitions on the production, placing on the market and use of chemicals

For each coating and agent, content of the volatile organic compound (VOC) is determined - ready to use

SRPS ISO 11890-2:2009- Paints and varnishes - Determination of the content of the volatile organic compound (VOC) - Part 2: Gas chromatographic method

SRPS ISO 11890-1: 2010- Paints and varnishes - Determination of volatile organic compound contents (VOC) - Part 1: Method of difference

Contents when there is a reactive diluent in the coating

SRPS H.C8.065 - NONE

SRPS H.C8.063: 1974- Paints and varnishes - Determination of volatile and non-volatile matter - REMOVED, REPLACED BY:

SRPS EN ISO 3251: 2012- Paints, varnishes and plastics - Determination of non-volatile matter content

SRPS EN 14059: 2009- Decorative oil lamps - Safety requirements and test methods - Ordinal restriction number 3 - Placing on the market of decorative oil lamps intended for general use is forbidden, unless manufactured in accordance with the standard

Nickel - standard not specified, but mentioned.

SRPS ISO 21461: 2015 - Rubber - Determination of aromaticity of oils in vulcanized compounds - ordinal number 50 - Polycyclic aromatic hydrocarbons

Azo Color Test Methods - Ordinal restriction number 43

SRPS ISO/TS EN ISO 17234-1:2010- Leather - Chemical tests for determination of particular azo colors in coloured leather - Part 1: Determination of specific aromatic amine derivatives from azo colors

ISO-TS ISO / TS EN ISO 17234-2: 2013- Leather - Chemical tests for determination of individual azo colors in coloured leather - Part 2: Leather - Chemical tests for determination of individual azo colors in coloured leather - Part 2: Determination of 4 -aminoazobenzene

SRPS EN 14362-1:2013- Textiles - Methods of determination of certain azo-based aromatic amine derivatives - Part 1: Detection of used azo-coloured or non-fibrous fibers

SRPS EN 14362-2: 2009 - Textiles - Methods of determination of certain azo-based aromatic amine derivatives - Part 2: Detection of used azo-colours by extraction

Paints, varnishes, coatings

SRPS ISO EN 927-1: 2014- Paints and varnishes - Coating materials and coating systems for wood surfaces exposed to external conditions - Part 1: Classification and selection-A / d

SRPS EN ISO 2808: 2011- Paints and varnishes - Determination of film thickness-A/đ

Additional-Amendments to the Regulations on Restrictions and Prohibitions. Regulation on Restrictions and Prohibitions of Production, Placing on the Market and Use of Chemicals that pose an unacceptable risk to the human health and the environment ("Official Gazette of RS" no. 25/15).

CONCLUSION

By applying the correct standard, improvisation and errors are reduced to the lowest level, time is saved in the execution of tasks and quality is ensured. Basically, the idea is that nothing is left to chance. Of course it is not possible to standardize everything, because if so, robots would long ago replace people or people would become robots.

Standards should provide frames, guidelines and tools, and technical accomplishment is left in the hands of organization. Standardization ensures that processes are arranged beyond any individual and are sustainable. Employees in organizations often oppose any introduction of standards, while a large number of managers experience this as an exclusive marketing category in order to present them on the market in the best light. The problem arises with insufficient education regarding the application of this "tool" and learning about benefits that proper application of standards can bring to business. World-renowned experts from various fields endeavor to transform their knowledge and experiences into good practices, and then into standard requirements and guidelines that can be successfully applied in all world organizations in order to maximize profits and ensure quality for users.

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WOMEN IN THE WORKFORCE – A CASE STUDY OF R. MACEDONIA

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Abstract

Over the past years, the transformation has occurred in the gender of the workforce in the EU and the Balkan countries. Women have entered in the labor market and increased the range of professions and sectors and have secured high positions within some companies and organizations. However, gender imbalances remain in the relation to the scope and form of employment and within the reward for the work they complete. In many ways, the organization of the workplace and the domestic division of labor retain the imprint of male influence. Despite worries about the progress in segregating employment, the value of women's work and the unequal distribution of domestic labor still persist. This paper made a comparative analysis by revealing the progress and challenges using recent research data and offers specific recommendations with a conclusion.

Keywords: Employment, Female employees, Comparative analysis, Region, Macedonia

INTRODUCTION

Nowadays, when the world is facing deep shifting in global challenges that affect both men and women, it is necessary to make transformation of their working tasks. Countries, irrelevant whether they have low or middle income, cannot lose social and economic potential on behalf of the gender equality. It takes ambitious policies that will enable transformation of the gender norms and relations in the society and at the work posts, and by that will help efficiently for solving structural inequalities. Gender gaps are present at higher paid jobs also. Female employees in Europe are less active participants in the total labor market force and they are facing inequalities in their economic status when compared to their male colleagues. In 2014 there were only 89 females to every 100 male employees. In many countries women in the workforce work significantly less hours than male labor market participants. Gender gaps are even more significant in the corporative sector positions. Since April 2015, on every 100 member of the corporative board of the big companies that are active on the public stock market, only 23 are females [1].

LITERATURE REVIEW

Gender gap in the labor market is an important social and developing aim [2-6]. Although public policies in many countries are showing progress in bigger advances in this area, they are only of partially encouraging nature. Big gender gaps at the work posts still exist combined with the higher rates of the economic growth and lower income inequality. Place in the household of women is partially explaining shorter working hours of female employees at the labor market-which is also manifested with the discrepancy in wages between women - mothers and women that are not mothers, better known as "motherhood wage gap". On contrary employed father are earning more than their not married counterparts [7]. Women in the labor market are facing higher risk of unemployment compared to men and with higher differences in the unemployment throughout the regions. Global unemployment rate estimated for 2015 shows rate of unemployment from 5.5% for males to 6.2% for females. In this respect, Minniti [8] and Minniti *et al*. [9] suggest that the ownership of women's businesses is behind men and why they are untapped "source of entrepreneurial energy." Bardasi *et al*. [10] note that women entrepreneurs are more concentrated in certain sectors such as retail and hospitality, while men are present in all sectors of the economy. Finally, the concentration in the informal sectors is explaining the gender gap in the productivity of the firms, resulting with productivity in different sectors [9,11]. North, South and Western Europe are most struck by the financial turmoil in terms of unemployment [5]. This can be the result of two main factors: financial crisis first struck the male dominated labor market sectors such as construction industry (for example in Ireland, Spain), that resulted in the growth of unemployment rate and narrowed employment gender gaps, and previously inactive married women that could participate directly in the labor force to compensate the loss in the family income, from their unemployed spouses [12]. In the course of the second phase of the adoption of austerity measures in many countries the result was loss or decrease of jobs in the public sector, that were female dominated, which was the reason why females were more struck by the financial crisis than their male counterparts [13,14]. Yet, some authors are emphasizing that this one should not be considered as a sign of improvement of gender equality, but as a fact that there is closing on the gap on these vulnerable positions as a consequence of the deterred labor market conditions [15,16].

THE SITUATION ON A GLOBAL LEVEL

As a consequence of the weak and insecure economic growth, the pace of improvement of the regional labor market shows certain slow down. Projected unemployment rate in the region is 9.1% for 2017, a decrease of 0.2% is noted compared to the values predicted for 2016 (Table 1).

Table1 *Projected unemployment for 2017/18 year*

Unemployment trends and projections, Northern, Southern and Western Europe, 2007–18

Country/region	Unemployment rate, 2007–18 (percentages)				Unemployment, 2016–18 (millions)		
	2007–2015	2016	2017	2018	2016	2017	2018
Northern, Southern and Western Europe		**9.3**	**9.1**	**8.9**	**20.2**	**19.7**	**19.4**
France		10.0	9.8	9.8	3.0	2.9	2.9
Germany		4.3	4.2	4.2	1.8	1.8	1.8
Italy		11.5	11.4	11.1	2.9	2.8	2.8
United Kingdom		4.8	5.0	5.3	1.6	1.7	1.8

Source: ILO Trends Econometric Models, November 2016.

Having in mind that the rate of unemployment decreased for almost 2% between 2013 and 2016, it is a considerable slowdown of the progress of the region towards the average growth rate before crisis that was set around 7.4% in 2008. Considerable decrease of the unemployment rate is expected in only few countries, including Croatia, Ireland, Netherlands, Portugal, and Spain. Nevertheless, there are only few countries that could achieve target growth rates in the next couple of years, especially in the United Kingdom [17]. Although women consist 46.1% from the employees in EU (28) female employment rates vary by country.

Table 2 *Percentage of Women in the Workforce at the global level [18,19]*

Country	Percentage of Women in the Workforce (2016)
European Union (28)	46.1
Austria	47.2
Belgium	46.8
Denmark	47.4
Finland	48.4
France	48.2
Germany	46.8
Greece	42.0
Hungary	45.8
Ireland	46.2
Italy	42.3
Netherlands	46.7
Norway	47.9
Spain	45.6
Sweden	48.0
Switzerland	46.9
United Kingdom	47.2

Higher inclusion of women in the higher levels of management can help to strengthen the efficiency of the companies by wider and better presentation of the changing demography of the workforce (OECD, 2012). Also, presence of the women employees of the high positions improves corporate performances and their profitable sectors, and that will help the support of the corporate investment and productivity, and it will help the ease of the potential growth. Such gender equality of the high corporate positions is achieved in the countries where women are related with the workforce with full time work posts. There are different assumptions for the deficit in the presence of women on high leading positions in the corporate world, as well as in politics. These are result from the existing stereotypes and norms about gender issues that are creating some glass ceiling, and for a shorter work time on women’s work posts [20,21]. Lack of presence of women on leader’s positions can only strengthen the biased perceptions about effectiveness of women on leaders positions. Women also solely do not believe in their capabilities to lead, because they rarely see other women on such positions [15,22]. They also could abandon their carrier road towards higher positions when do childbearing [23].

NATIONAL SITUATION AND PERSPECTIVES

Although in R. Macedonia gender equality is one of the rare values of the constitutional regime, and accordingly, there exists developed law and institutional framework that should enable realization of the higher gender equality in all domains of the social action. Adopted laws that regulate discrimination on the basis of the gender are: Law on equal possibilities for women and men, Law on prevention of corruption, Labor relations law. From essential importance is the Law on equal possibilities for women and men that gives directions for inclusion of the equal possibilities principle in the main courses of reorganization, improvement, development and the assessment of the political processes on all levels and phases. This law also sets the institutional framework, for setting up gender "machinery" that is useful to support and obtain all of the necessary processes for achieving full gender equality [24].

This law was changed and amended couple of times with the aim of harmonizing with the European acquis communitarian. Gender equality is adopted 2013-2010 with the aim of improvement of the possibilities of women and men in the all aspects of life in R. Macedonia. This strategy is adopted as a document which will provide "total equality framework of men and women as well as cross-sectional, horizontal and universal social and political priority". Furthermore, this strategy has essential steps and directions towards full realization in R. Macedonia. Following, the international courses, our country has adopted many international documents that are concerned with the gender equality and equal opportunities of men and women, and are adopted by the UN, and EU, Europe council and others [25].

ANALYSIS AND FINDINGS

Table 3 is showing the condition of the employment in R. Macedonia that is characterized with many unfavorable gender structures. This structure has not been changed for a long period of time, because instable socio-economic conditions in the country and non-coordination of the available and required profiles of the labor market. Women employment rate in R. Macedonia in 2016 is 33.8% and is considerably lower than their men counterparts with 52.3%. Unemployment rate in women is 22.7% and for men is 24.4%. Labor market active participation rate is 43.8% in women, and in men is considerably higher and is 69.2% [26].

Table 3 *Employed by economic status and gender, 2016 (Statistical review 2.4.17.02 /867, 2017:69.)*

Gender	Total	Economic status			
		Employed	Employer	Self-employed	Unpaid family worker
Total	723 550	548 937	32 003	95 364	47 211
Men	439 717	321 427	24 046	75 660	18 584
Women	283 834	227 546	7 957	19 705	28 627
Structure by gender in %					
Total	100.0	100.0	100.0	100.0	100.0
Men	60.8	58.6	75.1	79.3	39.4
Women	39.2	41.4	24.9	20.7	60.6
Structure by economic status in %					
Total	100.0	75.9	4.4	13.2	6.5
Men	100.0	73.1	5.5	17.2	4.2
Women	100.0	80.2	28	6.9	10.1

In Macedonia weak movements are registered in making some efforts to raise the awareness about the role of women into the economy and society in general. This is the case of the Association of Women Organizations in Macedonia. Moreover, several non-government organizations take active policy actions aimed to activate and involve women in the economic and political life of the country. Nevertheless, despite women's available human potential and capabilities for successful development of women entrepreneurship, strong governmental support is indispensable. More precisely, by providing material or non-material governmental support, women slowly but surely find their place in the Macedonian economy [11,27].

CONCLUSION

This paper has considered the possibility of strengthening the position of women in the process of employment and their economic status in R. Macedonia. Thus, there were identified main characteristics connected with the legal framework and the slow implementation and analyzed some impediments by which the legal implementation and adoption is facing. Gender equality improvement is of a key importance for the welfare of the society. Yet, women in the 21st century are continuing to face discrimination in many areas. International and national legal framework on the gender equality is dynamic and is fully regulating this matter. But in reality, there exists a need of practical implementation of all the documents dedicated to the gender equality and much more action for its effect. It is worth to mention that there are such legal acts that are seeking for the equal treatment of the two genders on ineffective way. Considering that the two genders are not in the same start position equal treatment will not give the expected results.

There exists reflective tendency for the improvement of gender equality through existing laws, strategies and action plans. Slow implementation of the policies for the gender equality and the absence of the political will for serious and responsible promotion of gender equality concept are contributing to the sustainment of gender inequality and discrimination. It is necessary to increase the consciousness of the businessmen for recognition of the gender inequality all with the aim that female employees getting fired in course of pregnancy and less paid labor, mobbing and violence on women to be part of the past. Strengthening of the position of women in every segment of the societal action is a required basis for prosperity and sustainability, because strong women mean strong society.

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A STUDY ON ENVIRONMENTAL AWARENESS PERCEPTIONS OF STUDENTS IN TURKEY AND BULGARIA

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Abstract

The article presents a diagnostic investigation of classroom self-assessment of 174 students in 8th grade of elementary school (92 from Bulgaria and 82 from Turkey). A method of assessment and self-assessment on 40 environmental terms was used. The skill of students to make right decisions about their environmental knowledge was studied. The influence of the differential effect of social status and academic achievement level upon self-assessment was revealed. Comparative analysis of the results from Bulgaria and Turkey showed that most of the students did not reflect critically upon their knowledge and did not evaluate it against school achievement standards.

Keywords: Academic achievement level, Gender, Self-assessment, Self-esteem, Social status

INTRODUCTION

Self-assessment, self-evaluation and self-esteem are very closely and hierarchically interconnected and very often used interchangeably. Self-assessment "is the process of critically reviewing the quality of ones own performance and provision" [1]. Student self-evaluation is both a process and a product, a form of narrative writing in which students describe their learning in a particular course of study and make qualitative judgments about it [2]. Self-esteem reflects a person`s overall evaluation or appraisal of her or his own worth" [3], "a pride in oneself, self-respect" [4], "a confidence and satisfaction a person has in him/herself " [5], "due respect for oneself, one's character, and one's conduct" [6]. All of the three depend a lot on assessment and evaluation, carried out by the teacher (internal evaluation) or by other institutions (external evaluation) [7].

The development of skills in the area of assessment is at the heart of a successful teaching and learning process [8-11]. Its aspects are studied by many researchers: meaning [8,9,12], principles [9,13,14], external and internal [15], formative [14,16], difficulties and shortcomings [17], importance for raising standards [13,11], interrelations with teaching and research [18,19], importance for formative and summative purposes [12,19], dependence on professional learning [20,21], requirements for efficacy [11,20,22], participation of students in the assessment process [23], learner-centered [22], performance in the classroom [10,11,13,19], role in motivation [24,25], comparison of peer- and self-assessment [26] self-assessment as a tool for personal learning and achieving academic excellence [25], student cooperation in learning and performance [20], teaching to and assessing with performance tasks result in understanding as a valuable contribution to assessment [27,28], development of practical materials for teachers [8,9,27], etc. Research is also directed to peer assessment that can be "usefully and meaningfully employed to factor individual contributions into the grades awarded to students engaged in collaborative group work" [26] and to the use of self-, peer and co-assessment [23].

The review of literature suggests that the use of a combination of different new assessment forms encourages students to become more responsible and reflective. Comparisons of the results of teacher and self-evaluation combined with critical and constructive discussion can help students to develop understanding and skills for self-regulated learning in pursuit for excellence.

MATERIALS AND METHODS

Participants in the investigation were 174 8^{th} grade students in four groups: two groups (T1 – 36 students and T2 – 46 students) from two Turkish schools in Bursa and two groups (B1 – 40 students and B2 – 52 students) from two Bulgarian schools in Sofia. T1 is representative of students with low social status, whilst T2 represents students of higher social status, studying in private elite school. The two Bulgarian groups were also different: students in group B1 had no specialized interest in biology whilst those in group B2 had a special interest in biology and had passed an entrance biology exam, choosing this area for future professional orientation. Our aim was to compare samples T1 and T2 with respect to the social status of the students and B1 and B2 regarding the students' interest in biology. And although the two groups from Turkey and Bulgaria were not identical they include students of the same age who study subjects with comparable contents.

Data collecting was done using self-assessment sheet written in child friendly language to aid children` understanding. The sheet contained 40 terms, chosen after careful analysis of the textbooks for sixth, seventh and eighth grades in Bulgaria and Turkey. The method has already been used and validated in a number of previous studies [29]. The validity of our survey instrument was 0.86, and the reliability was 0.77. The instrument was created in Bulgarian and adequately translated into Turkish language by E. Atasoy, a Bulgarian -Turkish bilingual.

The self-assessment sheet contained instruction and three tasks, formulated as follows: 1. Put a mark “K” (know), “H” (heard of) or “NH” (never heard of) for each concept, which best describes your opinion; 2. Choose 5 concepts that you know best and explain them. 3. Grade your knowledge and understanding (tick one) or using more precise mark from 1 to 5:

□ excellent	□ very good	□ good	□ poor	□ very poor

The self-assessment sheet was administered to the students for one school period of 45 minutes. The dependant variable of this study is the precision of self-assessment, i.e. the degree of approximation of students` self-assessment to the teachers` assessment and evaluation and the influence of social status, interest to biology and gender upon the precision of self-evaluation. The work sheets were collected and analyzed, using evaluation criteria, agreed upon prior to the test. Students were acquainted with the criteria for self-assessment. Statistical analysis was applied to the results.

RESULTS AND INTERPRETATION

The results were compared using statistical values (Table 1). The mean (X), mode (Mo) and median (Me) are different ways of finding the central value of the data in order to compare them. The results (Table 1) show that in all experimental groups with the exception of B2 group, in which the students had past an entrance exam in biology, the difference between evaluation and self-evaluation is significant. That means that preparation for and success at the entrance exam had been useful for development of understanding and skills for critical and precise self-assessment and self-evaluation. Academic self-esteem of these students was in correspondence with their achievement goals and learning standards. Students had special interests in biology and in the process of studying they competed between themselves, each trying to acquire higher professional knowledge and better marks. The rate of progress of individuals in B2 was high. They also learned from better qualified teachers, often lecturers from the university [20]. Biological education in this school is set on higher standards, which are nearer to the entrance exams for the universities, than the standards for the ordinary secondary schools. The results are reflection of pupils` attainment. Students had a real interest in their qualification as it opened doors for them to the next stage of their learning [12]. Self-evaluation is an empowering process developing skills and reflective learning.

Table 1 *Comparative statistical analysis of evaluation and self-evaluation of the variables*

Variables	X	Mo	Me	S2	S	V	Sx	T
B1 Evaluation	3.38	3.4	3.4	0.55	0.74	0. 22	0.12	4.82/ 1.98*
B1 Self-evaluation	4.14	4	4	0.44	0.66	0. 16	0.10	
B2 Evaluation	3.89	4	4	0.42	0.65	0. 17	0.09	1.22/ 1.98*
B2 Self-evaluation	4.05	4	4	0.48	0.69	0. 17	0.10	
T1 Evaluation	2.55	3	2.6	0.37	0.61	0. 24	0.10	8.26/ 1.98*
T1 Self-evaluation	3.72	4	4	0.37	0.61	0. 17	0.10	
T2 Evaluation	2.82	2.6	2.6	0.48	0.69	0. 24	0.11	4.51/ 1.98*
T2 Self-evaluation	3.48	4	4	0.52	0.72	0. 21	0.12	

$p < 0.05$

Variance (S^2) and standard deviation (S) are measures of variability. Standard deviation is the most commonly used measure of spread. In B1 variance and standard deviation for evaluation are higher than for self-evaluation, which shows that evaluation marks are more variable. This can be explained with the higher precision of teachers and the use of pre-developed criteria. Students relied predominantly on their intuition and self-esteem. In the other three groups the SD (S) for the distribution of the evaluation marks is either smaller or equal to SD of the self-evaluation marks, which shows that they are clustered more closely to the mean. The coefficient of variation (V) is a measure of dispersion of a probability distribution. Except in B2 group in the other groups V is higher for evaluation than for self evaluation, which confirms the explanation about the higher precision of teacher evaluation. Sx (SEM), the standard error of the mean, provides simple measure of uncertainty in a value and quantifies the accuracy of the true mean of the evaluation and self-evaluation marks. Student t distribution for the comparison of the results from evaluation and self-evaluation in B2 is less than 1.98, which is the standard value at $p < 0.05$ and $f = 52 + 52 – 2$. But in all other groups it is higher and proves that the difference between evaluation and self-evaluation is significant. This could be the result both of lack of knowledge and lack of skills for critical self-assessment.

Social status of student has an indirect effect on self-assessment and self-evaluation. Having better financial resources, students in T2 group were able to afford better education than students in T1 group. But their higher attainments were also the result of greater efforts in studying and more critical approach to self-evaluation. Academically successful students (B2 and T2) showed a more critical view of themselves and students with more modest academic abilities (B1 and T1) compensated for their academic underachievement by elevating their general self-esteem and using self-protective enhancement [30].

Nevertheless objective evaluation in B2 and T2 was higher, which could be due to school climate favouring learning, academic achievement and self-responsibility for success. It is proved by the values of S, V and SEM (table 1). Overestimation and underestimation by one point predominated. Self-regulation and expert performance in B2 and T2 was higher due to reflection and deliberate practice [20,25]. Self-monitoring requires more time and effort [23], but the students in B1 and T1 were not taught to give it. Educational assessments and self-assessments are very essential for feedback and feedfoward to raise levels of attainment and empowering lifelong learning [27,30]. Excellent academic achievements raise students` self-esteem [30].

CONCLUSION

The social status and the entrance exams to school are both very essential in developing skills for correct self-evaluation. Obviously school environment and school practices favored self-evaluation for learning, not only of learning. Students in B2 and T2 had better understanding of their attainment goals, which helped them in self-evaluation. Self-evaluation was not regarded as a process where both teachers and student analyze their work and acquire self-assessment as a result. Self-evaluation skills are the condition and result of education, the condition of self-regulated life-long education as they develop personality and regulate behavior [18]. The use of self-evaluation techniques allows teachers and students to reflect on practice and improve effectiveness. Effective self-evaluation provides a great sense of ownership of the evaluation process and should experience a greater consideration in school practice [14].

Students need understanding and practice in self-assessment and self-evaluation in order to develop their objectivity and self-regulated learning and to acquire proper self-esteem skills and attitudes. Self-assessment should be incorporated systematically into teaching strategies and practices at all levels and only in this way it can provide informed feedback to pupils, develop and sustain skills for objective self-evaluation, i.e. corresponding to teachers` and external assessment and to school and personal goals. The purpose of assessment is to improve standards, not merely to measure them and that should be the case for all schools not only for special schools.

Assessment and self-assessment for learning should be the leading strategy in teaching in order to help students understand their achievements and shortcomings and to give them guiding principles to build on them their successful learning. Peer and co-assessment have not found yet their ways to school practice in the assessed schools, but they can help students understand their responsibility for their own achievements [27] and motivate them [24]. That of course needs competent teachers and specific experiences as well as school climate and evaluation tools [9,11,14,17,22,26]. Objective evaluation and self-evaluation is needed to prepare students for competition in Europe and should make their ways to school planned practices [12,18,21,30].

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PERMANENT ECOLOGICAL AND HEALTH EFFECTS OF NATO AGRESSION IN FRY - ONE VIEW

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Abstract

The introductory part briefly presents the situation of NATO aggression on the FRY. The characteristics of the air raids and the effects of the missiles, which were used on this occasion, with the emphasis on the basic characteristics of depleted uranium ammunition have been presented. The second part deals with the spatial arrangement of fired missiles by calculating the coordinates obtained from NATO forces. On the basis of the available data, the number of missiles fired at populated areas or immediate vicinity, and the amount of depleted uranium expressed in kg per each targeted settlement, were calculated. We also divided the spatial distribution of the missiles in the river basins for a more complete explanation of the adverse effects on the terrain, surface waters and subterranean waters. The third part covers the ecological and health consequences of the use of depleted uranium ammunition. Radioactive and toxic effects of depleted uranium affect the radioactive and chemical contamination of the natural environment and cause instant and delayed health problems for people in the contaminated area. On the basis of available data, complex, insufficiently investigated, hardly predictable and long-lasting effects of depleted uranium on the health of the population are presented.

Keywords: NATO Aggression, Depleted uranium, Health effects, Ecology

INTRODUCTION

The aim of this work is to point, without going into political reasons and implications, to the immense consequences caused by the NATO aggression on the FRY in 1999. The consequences are such that we can outrightly talk about ecological catastrophe with consequences on the health of people that cannot yet be fully seen.

During the air raids on the Federal Republic of Yugoslavia from March 24 to June 11, 1999, NATO forces used depleted uranium ammunition (DU). The air raids' focus was on the territory of Kosovo and Metohija (KM) and South Serbia. According to NATO data, ammunition with the DU was used in the territory of KM, especially on the border with Albania, where about 31,000 missiles were fired, in the south of Serbia (Presevo, Bujanovac and Vranje) between 3,000 and 5,000 missiles and in Montenegro (Lustica peninsula) about 300 missiles, in total over 11,500 kg DU. The FRY army has reported that there were about 45,000 missiles or 15 tons of uranium. The Russians estimated that 90,000 missiles, or 30 tons of uranium, were fired [1]. It is not known whether the cruise missiles ("tomahawk"), which targeted the economic and other targets in the FRY, had depleted uranium filling.

Depleted uranium is a by-product (waste material) in the production of nuclear fuel, where the ^{235}U is separated from natural uranium during the so-called process of "enrichment", and depleted uranium ^{238}U [2] occurs as a waste product. By enriching natural uranium, large quantities of depleted uranium (DU) are produced. For example, the production of 1 kg of 5% enriched uranium requires 11.8 kg of natural uranium and leaves about 10.8 kg DU with a residue of only 0.3% [3]. The density of the OU is about 19.07 g/cm^3 (1.7 times the denser than the lead and 2.42 times the thicker of the iron), contributing to the great breakthrough power. This, in addition to its low price, makes it easy to access and suitable for use primarily in the military industry in which it is used for the production of anti-tank ammunition and ammunition for action against established objects, but also for the production of tank armors and some types of cruise ships missile "Tomahawk" to increase the stability of their flight. It is believed that between 17 and 20 countries have weapons that include depleted uranium in their arsenals. These include the United States, Great Britain, France, Russia, China, Turkey, Israel, Saudi Arabia, Bahrain, Egypt, Kuwait, Pakistan, Thailand, Iraq and Taiwan. Only the United States and Great Britain have recognized the use of weapons with the DU.

Spatial-temporal distribution of depleted uranium missiles in the territory of FRY

The map of the NATO air force action contains 112 targets in 91 locations targeted by missiles with DU. 98 hits were performed at 81 locations in KM, 12 were hit at 9 locations in the Republic of Serbia outside the territory of Kosovo and Metohija, and two were hit on one location in Montenegro [4]. Two missiles were registered in Albania and one in Macedonia.

Table 1 *Number of missiles with DU in populated places*

	Populated place	Number of missiles
1.	Orahovac	1170
2.	Djakovica	7286
3.	Klina	571
4.	Glogovac	705
5.	Presevo	607
6.	Bujanovac	3074
7.	Prizren	8642
8.	Decani	5672
9.	Podujevo	740
10.	Stimlje	305
11.	Suva Reka	745
12.	Leposavic	570
13.	Srbica	268
14.	Kosovska Kamenica	184
15.	Gnjilane	559
16.	Vitina	473
17.	Pec	1695
18.	Pristina	375
19.	Kosovska Mitrovica	847
20.	Novo Brdo	423
21.	Urosevac	2235
22.	Istok	422
23.	Montenegro (Boka Kotorska)	600
24.	Albania	485
25.	Macedonia	375
	Total	39028

Most missiles with depleted uranium hit the territory west of the Pec-Djakovica-Prizren area, the area around Klina, the vicinity of Prizren, and the area north of the Suva reka / Urosevac line (Table 1). However, many actions that used ammunition with the DU were outside these areas.

It is assumed that the targets were tanks of the FRY army that were mostly deployed along the border with Abania (near Prizren, Djakovica and Pec) and along the administrative border with Serbia, around Vranje and Bujanovac. More than 15 sites affected by the DU were located on the road of Djakovica - Zrze, then on the route Decane - Rznic - Prilep - Junik (more than 10 locations). In the territory of the Federal Republic of Yugoslavia outside the territory of KiM it was established that the targeted sites were: a repeater tower on Plackovica north of Vranje, Borovac south of Bujanovac, Cerenovac southwest of Bujanovac, Bratoselce northeast of Presevo, Reljan east of Presevo and the Azra fortress on the Lustica peninsula in Montenegro.

NATO forces did not use missiles with the OU in the first 13 days of total of 78 days of aggression. In the final sum more than half the aggression time (40 days) ammunition with the DU was used. It should be emphasized that the half of total number of attacks with the DU has been executed in the first 10 days of the bombardment, during the period when the political agreement between the Government of the FRY and the negotiating team Ahtisari-Cernomirdin already was reached on the end of the war and the beginning of the withdrawal of the FRY army from the territory of KM. Over 54% of the projectiles were fired then. The most projectiles were fired on June 6 -3,957, June 7-3,090 and June 8-3,390, a total of 10,437 or 26.7%. During 13 days of aggression, over 1,000 projectiles were fired daily (Figure 1). Furthermore, during the indicated period, the bombs with the DU were fired with no selection, not only on military but also on civilian targets, such as TV repeater tower on Plackovica, only 3 km away from the center of Vranje.

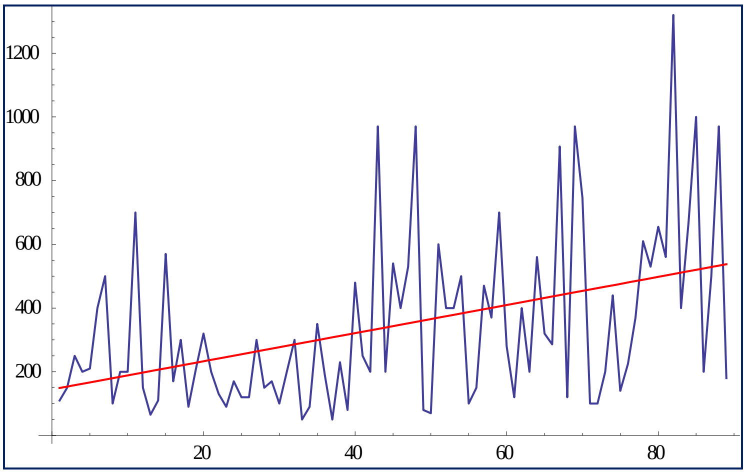

Figure 1 *Display of the number of missiles projected with the DU during aggression (the red line shows the trend of the projected missiles with the DU)*

The environmental and health effects of NATO aggression on the FRY

It's been 19 years, and accurate and official data on the resulting and possible consequences of using depleted uranium (DU) missiles and other chemical and radioactive materials that are dangerous to human health during the NATO aggression against the Republic of Yugoslavia (FRY) have not been available to the scientific and professional public in 1999. The only studies so far have been limited to military personnel with varying levels of exposure. So far, the most serious research in our country has been presented in a monograph [5].

The number of fired missiles does not indicate how many of them hit the target, because in this case the effects of pollution are different. Air pollution starts when a fired missile hits a target. Part of the ammunition with the DU forms a cloud of flammable dust consisting of particles of various oxides, size from 0.2 to 15 microns, as well as large fragments. The proliferation of gaseous oxides by long-range airflow causes a delayed exposure to small amounts of radiation to the global population. Kosovo is known as an extremely windy area [6]. According to the data of the Pristina meteorological station, the average wind strength is higher than 6 degrees on the Beaufort scale and in some months it is higher than 10 degrees. The direction of the wind and the wind strength are affected by the air pressure and the configuration of the relief. The most frequent winds in Pristina are the northern wind (17.3%), then the northeast (16.6%), followed by the southwest (7.4%) and the south (6.4%). In the Metohija valley (Prizren and Pec, the most frequent winds are from the southwest (13.8%) and the west (12.3%). [7] This means that frequent and strong currents from the windy areas of the entire region spread dangerous particles to a wide the area of the Balkan Peninsula. In mid-June 1999, scientists from Greece published the results that indicated that the radiation in that region was increased by at least one quarter each time a wind came from the direction of Kosovo (north wind). Similar research was carried out by scientists from Bulgaria who came to the data that increased radiations of eight percent were recorded over their country and up to 30 percent over the FRY [8]. It is believed that, depending on meteorological conditions, 'the range of radioactive particles of DU aerosol is practically unlimited'[9]. Some authors connect the increase of the radioactivity of the atmosphere with forest fires. The uranium in unexploded or scattered exploded projectiles in contact with the outside environment affects the delayed emission of ionizing radiation for years [10]. The reaction of uranium with oxygen causes self-ignition. It is believed that frequent fires are caused by flammable parts of depleted uranium ammunition. The increased frequency of forest fires corresponds to the periods of increased radiation after the bombing. It is thought that this type of fire can increase contaminated areas by scattering radioactive particles [11].

Unexploded missiles contaminate soil, water and plants, which is a permanent contamination, with radioactive particles which remain in the natural environment for a long time.

The time of their complete decomposition is from 25 to 30 years [12]. Contamination of soil and water depends on the geological composition of the area being targeted. Kosovo and Metohija is characterized by a complex geological structure in which there are three types of rock; old resistant and solid crystalline mass with limestone admixtures, then neogenic lake sediments and ultimately alluvial deposits that fill the valleys. On topographic surfaces of solid geological composition complete or ammunition residues with DU were found. The projectiles, when struck in a solid surface, were rejected or turned away and held back on the surface, so it was relatively easy to spot them. The surface layer of the soil under them is contaminated with fine particles of the DU. If the missile strikes in soft lake sediments or river deposits, it penetrates to different depths depending on the height of the shot and the angle of penetration. They were found at depths from 20 to over 100 cm. Radiation was detected 5-7 cm below the surface. Contamination is point source and these missiles are very difficult to find. In the soil samples, the activity of DU 5,580-23,5000 Bq/kg was measured, which is more than 1,100 times more than the defined lower limit [13].

The behavior of penetrators with depleted uranium was studied by Erikson and associates [14] who confirmed that depleted uranium penetrators are mainly corroded in the hydrated U

(VI) oxide, a highly water-soluble uranyl carbonate. Following the construction of uranium ions and entry into groundwater, depleted uranium, through the food chain, receives an unknown further flow and the inability to estimate its final stop.

In the monograph [5], the biological effect of depleted uranium on the human organism is studied in detail. The so-called, Petkau effect, Canadian scientist Abram Petkau experimentally proved in 1972 that small and slow doses of radiation cause greater toxic effect than large doses. The most common consequences for human health are thyroid gland disorders, malignant diseases and fetal anomalies, not only in war areas, but also in areas thousands of miles away.

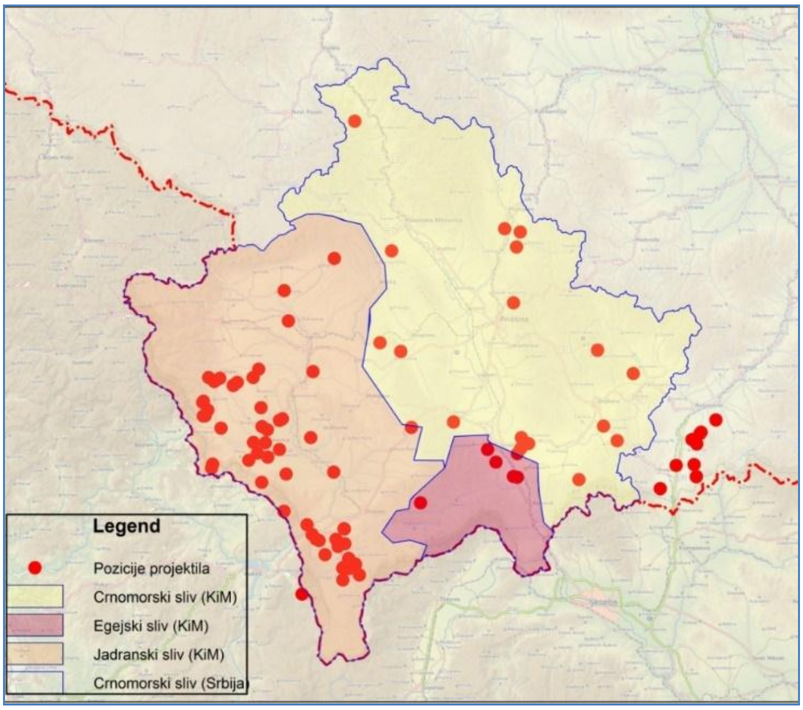

Figure 2 *Disposition of fired missiles in river basins*

Table 2 *Number of missiles in river basins*

nu	Basin		Number of residents	Total basins	%	Number of missiles
1.	The Adriatic Sea basin	KM	70	74	66.07	25786
		Albania	2			
		Montenegro	2			
2.	The Aegean Sea basin	KM	5	6	5.36%	2092
		Macedonia	1			
3.	The Black Sea basin	KM	19	32	28.57%	11150
		Serbia	13			
		total	112	112	100%	39028

CONCLUSION

It has been proven that the use of ammunition with DU caused long-term dangerous chemical and radioactive pollution in our country. The risk of contamination can be difficult to control and localize. Milligram of DU, with two descendants during the decay, discharges about one billion of radioactive particles in a year. Pollution of water and soil increases the danger with the flow of time. Water contamination can be expected by some authors after 50 years of application, with maximum values after 100 years and the tendency of long-term presence at high values afterwards. In addition to carcinogenic diseases that occur after 30 years as a result of the carcinogens, genetic changes can occur which lead to degeneration and reduction of offspring. Therefore, long-term environmental monitoring and medical surveillance of the population are required.

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PHOTOCATALITIC DECOMPOSITION OF DICLOFENAC, IBUPROFEN AND KETOPROFEN BY ZnO FOR WASTEWATER TREATMENT

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Abstract

Photocatalytic decomposition of diclofenac, ibuprofen and ketoprofen with ZnO powder was investigated in aqueous solution in batch mode, under UV irradiation. Efficiencies of photodegradations after 90 minutes were 65.87%, 54.22%, 98.52% for diclofenac, ibuprofen and ketoprofen, respectively. Although the high efficiency of photodegradation was detected the results also indicated that there is a need for more detailed and systematic investigations examining the role of catalyst conditions and chemical nature of pollutants.

Keywords: Zinc-oxide, Diclofenac, Ibuprofen, Ketoprofen, Photocatlysis

INTRODUCTION

The photocatalytic degradation of pharmaceutically active compoundsis of a great importance considering that pharmaceutical pollutants are persistent contaminants in aquatic media and that conventional treatment plants are inefficient for their removal [1-3]. Unlike the vast majority of water pollutants (phenols, phthalates, PCBs etc.) pharmaceutical molecules bear certain differences in their molecular structure which render them less amenable to photodegradation.

Among a wide range of pharmaceuticals, synthetic, non-steroidal anti-inflammatory drugs (NSAIDs) are one of the most frequently detected pharmaceutical residues according to their widespread availability. Diclofenac (2-(2,6- dichlorophenylamino)phenylacetic acid, DCF), ibuprofen (**α**-Methyl-4-(isobutyl)phenylacetic acid, (±)-2-(4-Isobutylphenyl)propanoicacid) and ketoprofen (2-(3-Benzoylphenyl)propionic acid) are some of the commonly used NSAIDs and some of the most frequently detected emerging pollutants (EP) in water matrix.

Among the methods that have been developed for water disinfection, advanced oxidation processes such as heterogeneous photocatalysis appears as an emerging technology for the decomposition of most of the organic pollutants. Over the last years, ZnO appears as a strong rival to previously dominant candidate for wastewater treatment: TiO_2 [4]. This stems from the fact that despite both oxides are wide band gap semiconductors and hence absorb only a small (~5%) fraction of the solar radiation, ZnO exhibits least two orders of magnitude higher mobility of the photoexcited electrons than that of TiO_2 [5]. Our previous research [6] has shown that ZnO has a high potential in photocatalytic decomposition of naproxene.

The aim of the present study is to investigate the possibility of photocatalitic decomposition of selected pharmaceuticals by using commercially available and therefore affordable ZnO powder.

MATERIALS AND METHODS

Zinc-oxide used in present study was a commercial ZnO, Sigma Aldrich, purity 99.9%, particle size <1μm.

Diffuse reflectance spectra of obtained samples were recorded by a double-beam UV/VIS/NIR Perkin-Elmer spectrophotometer (model Lambda-950) in the spectral region from 300 nm to 1500 nm using an integrating sphere. Spectral parameters were used for estimating the optical band gap of the materials.

The photocatalytic decompositions of chosen pharmaceuticals were carried out at ambient temperature in aqueous solution in batch mode. The stock solution of the analyzed pharmaceutical was prepared by dissolving 5 mg of standard in 25 ml of acetonitrile (200 mg L^{-1}). Distilled water was used as the aqueous model. The aqueous solution was stirred for 1 h in the dark to establish adsorption-desorption equilibrium between the pharmaceutical and photocatalyst before being irradiated. The aqueous solutions were exposed under continuous UV irradiation. The source of the UV light was high-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335, and 366 nm, with maximum emission at 366 nm). The solutions were stirred with the aid of a magnetic agitator at 130 rpm. In order to investigate the change in composition of the investigated pollutant, aliquots were collected at certain time intervals (5, 10, 20, 30, 40, 50, 60 and 90 minutes). Each sample was filtered through filter paper (diameter 90 mm) in order to separate the ZnO particles from the solution. After the filtration step, 1 ml of sample was transferred into 2 ml vials.

A HPLC (high performance liquid chromatography) with diode array detector (Agilent 1260 series) was used for the measurement of each specific pharmaceutical concentration after photocatalytic degradation.

RESULTS AND DISCUSSION

The UV–Vis diffuse reflectance spectra of the ZnO powder enabled the determination of the optical band gap, Eg, of 3.29 eV [6], by applying the analysis of the Kubelka–Munk theory. This value indicated that photocatalytic decomposition can be carried out under the UV irradiation.

The PC activity of ZnO was evaluated by the photodegradation of diclofenac, ibuprofen and ketoprofen in distilled water under UV irradiation. The evolution of chosen pharmaceuticals photocatalytic degradation rates as a function of time for the investigated pharmaceuticals are shown in Figures 1-3. We observe that efficiencies of photodegradations after 90 minutes are 65.87%, 54.22%, 98.52% for diclofenac, ibuprofen and ketoprofen, respectively.

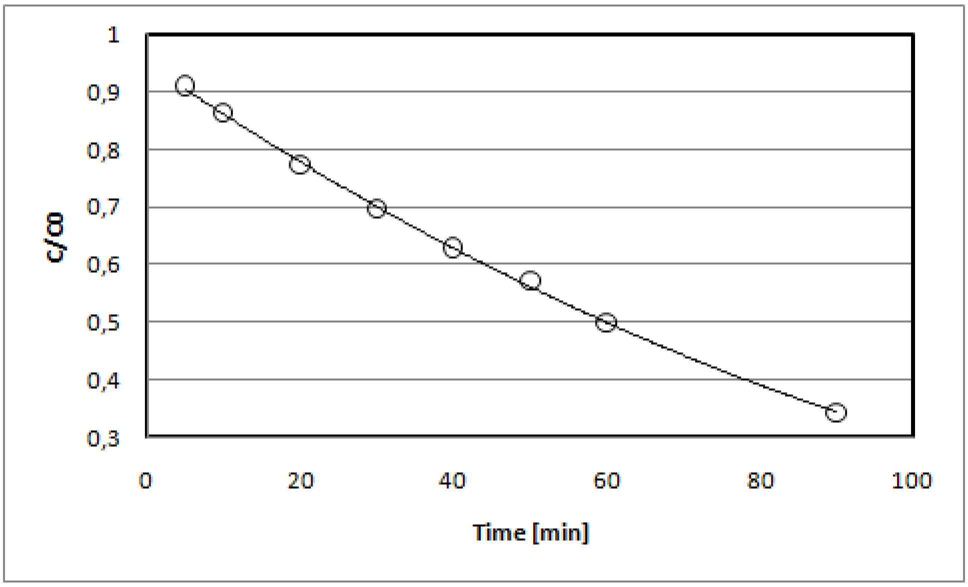

Figure 1 *Kinetic of photocatalytic degradation of diclofenac by ZnO (the line is used as guide to the eye)*

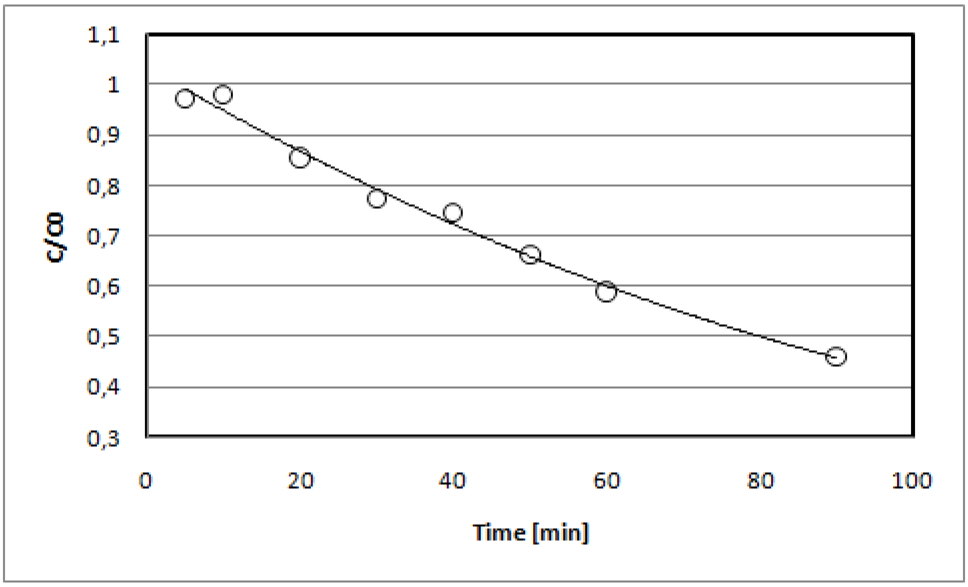

Figure 2 *Kinetic of photocatalytic degradation of ibuprofen by ZnO (the line is used as guide to the eye)*

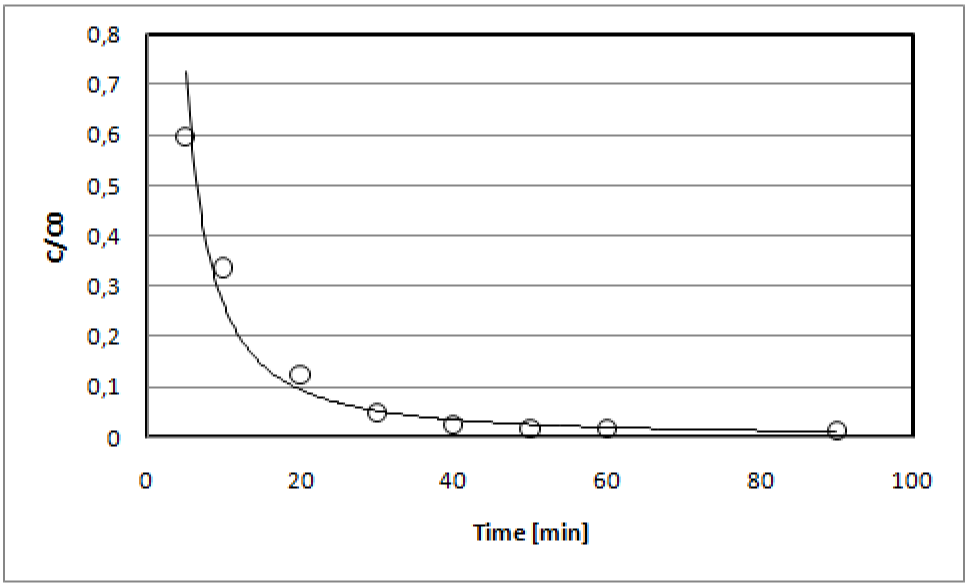

Figure 3 *Kinetic of photocatalytic degradation of ketoprofen by ZnO (the line is used as guide to the eye)*

As we have recently published in [6], the commercial ZnO (Sigma Aldrich, purity 99.9%, particle size <1μm), also used for present study, comprise particles of complex shapes where needle-like shapes (nanorods) dominate over particles with irregular shapes (Figure 4). The ZnO powders containing nano-particles must be carefully studied regarding their potential negative impact on environmental systems.

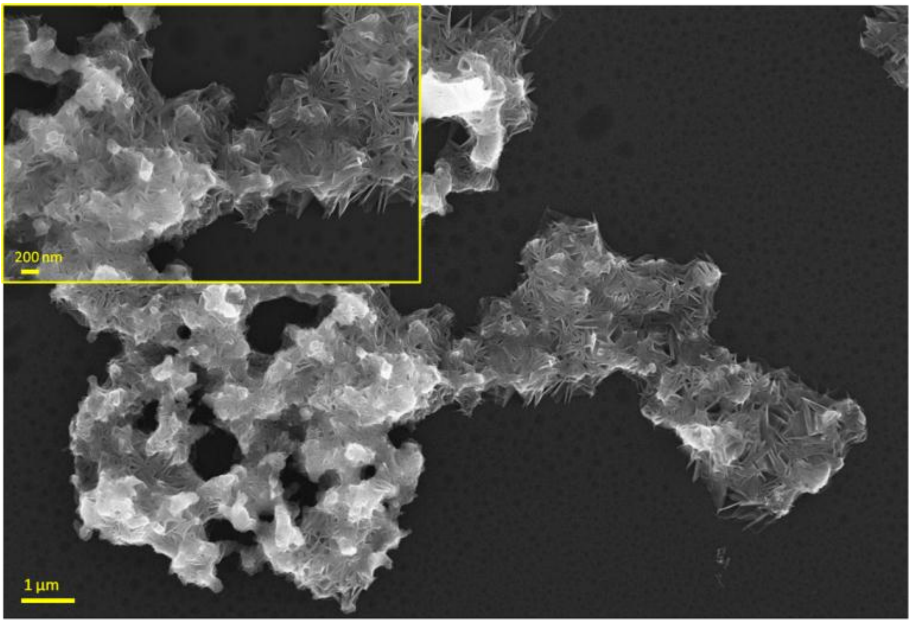

Figure 4 *Representative FE-SEM image of the ZnO powder [6]*

Currently available data in the literature clearly demonstrate that release of nanoparticles into environment, especially of ZnO, may represent a risk to aquatic biota As for other nanoparticles, ZnO may also be toxic for some microorganisms, making them potential antibacterial, antifungal, and antiviral agents.

Although safety measures have been assumed during industrial production, storage, and removal of these nanomaterials, a constant monitoring of possible risks for aquatic life and ultimately humans is needed [7].

Imobilisation methods are currently being investigated for prevention of ZnO releasing into environment. ZnO nanoparticles have been successfully added into the various polymer matrices such as Polyvinyl alcohol, Polypropylene, Polystyrene, Low density polyethylene, Polycaprolacton, Polyester imide, Polyamide–imide, Silicon rubber, Polymethylmethacrylate, Polyimide, etc. [8-10]. At present, in order to prevent the release of nanoparticles, the immobilization materials are being investigated by the authors, with the aim to obtain a material for easy handling and practical application without significant influence on photocatalytic efficiency of ZnO.

CONCLUSION

Although a future research should be done for optimization of photodegradation process (influence of concentration of catalyst, time of irradiation, initial concentration of investigated pollutant, effect of pH value, water composition, identification of byproducts etc.), photocatalytic decomposition by ZnO powders could be considered as a promising method for removal of diclofenac, ibuprofen and ketoprofen. The results the PC efficiency is determined by the chemical nature of the pharmaceutical and no universal rules can unequivocally be settled.

Bearing in mind possible implications for aquatic biota and humans, further investigations of ZnO toxic effect, constant monitoring and development of immobilisation materials are needed for their prolonged use.

ACKNOWLEDGEMENT

The presented research is partly financed within a project of the Government of Vojvodina “Synthesis and application of new nanostructured materials for the degradation of organic pollutants from municipal landfill leachate in Vojvodina“ 142-451-2479/2017-01/02. Authors want to acknowledge Dr. Spyros N Yannopoulos from FORTH/ICE–HT, Patra, Greece, for FE-SEM image.

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FOOD CONTACT MATERIALS SAFETY, REGULATORY ASPECTS AND OVERVIEW OF THE RESULTS OF CONTROL

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Abstract

Food contact materials (FCM) present all materials and articles intended to come into contact with food, such as packaging and containers, kitchen equipment, cutlery and dishes. These can be made from a variety of materials. The safety of food contact materials must be evaluated as chemicals can migrate from the materials into food. The materials must be manufactured in compliance with our and also with EU regulations, including good manufacturing practices. So that any potential transfer to foods raise safety concerns, change the composition of the food in an unacceptable way or have adverse effects on the taste and/or foods odor. In this paper, we want to present the results of control of food contact materials in three years period from 2015 to 2017. The control study included 874 samples made from different materials and it showed that only 44 of them were not in compliance with law. The most common reason for that was the change in sensory characteristics as well as total migration. Increased total migration causes non-compliance with law and requests further analysis.

Keywords: Food contact materials, Safety, Migration, Testing conditions

INTRODUCTION

The purpose of this paper is to show requests for safety assesment of food contact materials.General requierments, total migration and specific migration, change in sensory properties and labelling.

General conditions have been given in Article 3 of Regulative 1935/2004/EC and they included next: ”Materials and articles, including active and intelligent materials and articles, should be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could: endanger human health or bring about an unacceptable change in the composition of the food and bring about a deterioration in the organoleptic characteristics thereof. The labelling, advertising and presentation of a material or article shall not mislead the consumers“ [1].

Materials which have been used in contact with food are separated in 17 groups (active and intelligent materials and articles, adhesives, ceramics, cork, rubbers, glass, ion-exchange resins, metals and alloys, paper and board, plastics, printing inks, regenerated cellulose, silicones, textiles, varnishes and coatings, waxes, wood).

Table 1 *Requests for testing certain contaminants and regulative in correlation with material type*

active and intelligent materials		Regulation EC 450/2009
adhesives	Depending on type of adhesive	
ceramics	Pb, Cd	
cork	PCP, triclorophenols, pesticide residue, mycotoxins	
rubbers	N-nitrozamines, primary aromatic amines, formaldehyde, ditiocarbamates, BT, MBT, Pb, As, Zn	
glass	Pb, Cd	
ion-exchange resins	-	
metals and alloys	Cr, Ni, Mn, Pb, Cd, Hg, Al, ...	
paper and board	Pb, As, formaldehyde, PCBs	
plastics	PAAs, formaldehydes, BPa, phthalates, overall migration	Regulation EC 10/2011
printing inks	As, Pb, Cd, Hg, Ba, Cr, Sb, Sn, PAHs, PAAs, ITX, BP, mineral oils	
regenerated cellulose	formaldehyde	
silicones	volatiles	Directive EC 42/2007
textiles	Printing inks, bleaching and impregnation	
varnishes and coatings	PAAs, formaldehydes, phenols, Zn, overall migration	Regulation EC 1895/2005
waxes	PAHs	
wood	Anti microbial agents, humidifying agents, formaldehyde	

Until now, only four groups of materials have been regulated by specific EU measures: plastic, recycled plastics, ceramics and regenerated cellulose films. Other parameters that have been presented in Table 1 were prescribed by national law or certain acts (for example metals and alloys) [2-5].

In our country the current law is the *Law of consumer goods safety* (Official Gazette of RS No 92/2011), actually *Act on conditions concerning consumer goods safety attended for the market* (Official Gazette SFRJ No. 26/83-18/91) [2,3]. For testing some FCM types certain national standards protocols are in use.

MATERIALS AND METHODS

In this paper we will present the results of the safety controls in the period of three years, from 2015 to 2017. Control of FCM was performed in accordance with Regulation with force in our country. Safety control was included 874 samples in total of which 266 was plastic material samples, 264 metal material samples, 161 paper material samples, 101 glass material samples, 40 elastomer material samples, 26 ceramic material samples, 9 wood material samples and 7 samples with the enamel layer. Different materials of samples are shown on Figure 1.

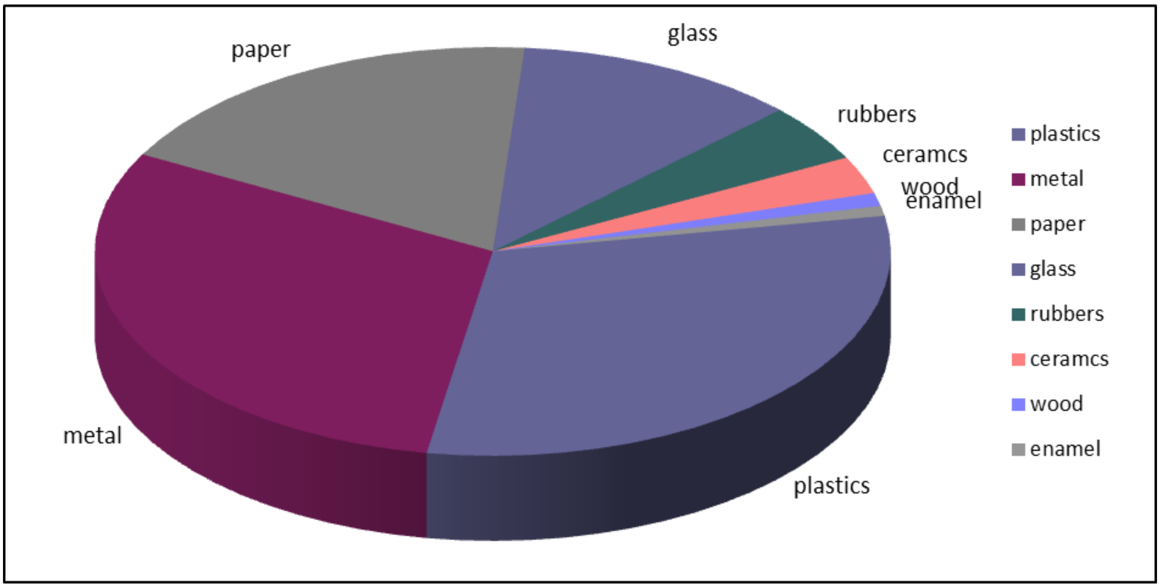

***Figure 1** Different materials that had been part of control in period from 2015 to 2017*

Sensory analysis has been done for all samples determined in accordance in aligned with SRPS EN 1230-1:2008 [6].

Analysis of plastic materials included determination of overall migration and specific migration of metal and metalloids while for some samples the specific migration of phthalates and formaldehyde was included. Total migration determined in accordance in aligned with SRPS EN 1186-1:2008 [7]. Migration testing is usually done by using various food simulants (for example, 10% ethanol for alcohols, 3% acetic acid for acidic food). Testing temperature and duration also vary depending on food package use conditions.

For metal, glass and ceramic materials specific migration of different metals were done [5]. Specific metal and metalloids migration for all samples was determined by AAS flame technique.

For paper and elastomer we determined metals and metalloids. In paper materials formaldehyde was determined and for some samples even PCBs. Formaldehyde determination determined in accordance in line with SRPS EN 1541:2008 [8].

For samples with enamel layer we determined the total migration and specific metal and metalloid migration. For wood material samples we determined the formaldehyde migration.

Specific metal and metalloids migration for all samples was determined by AAS flame technique.

RESULTS AND DISCUSSION

Only 5 percentage of all tested samples in period between 2015-5017 was marked as not-compliance. In 2015, 269 samples were tested and 30 of them were unsafety and from that number 66.6 % was unsafety due to sensor characteristics change.65% had noticeable residual scent, while 35% had sensory characteristics change after contact with food simulants. The second reason of the not compliance was the high concentration of metals while for 7% of unsafety samples was determined total migration increase. In 2016, 301 sample was tested and 8 were marked as not-compliance. 50% had sensory characteristics change and 50% had noticeable residual scent after testing, contact with food simulant. The second reason for unsafety was specific metal increase and 20% samples had total migration increase.

In 2017, 304 samples were tested and 2% were in compliance. 83% of the unsafe samples had specific metal migration increase and one sample beside specific metal migration increase had sensory characteristics change. The second reason for unsafety (50%) was specific migration of metals increase and 20% had total migration increase. In period between 2015-2017 50% of unsafety samples were from plastic materials, 23% from metal, 11% from elastomer, 7% from paper and 4% from glass and enamel.

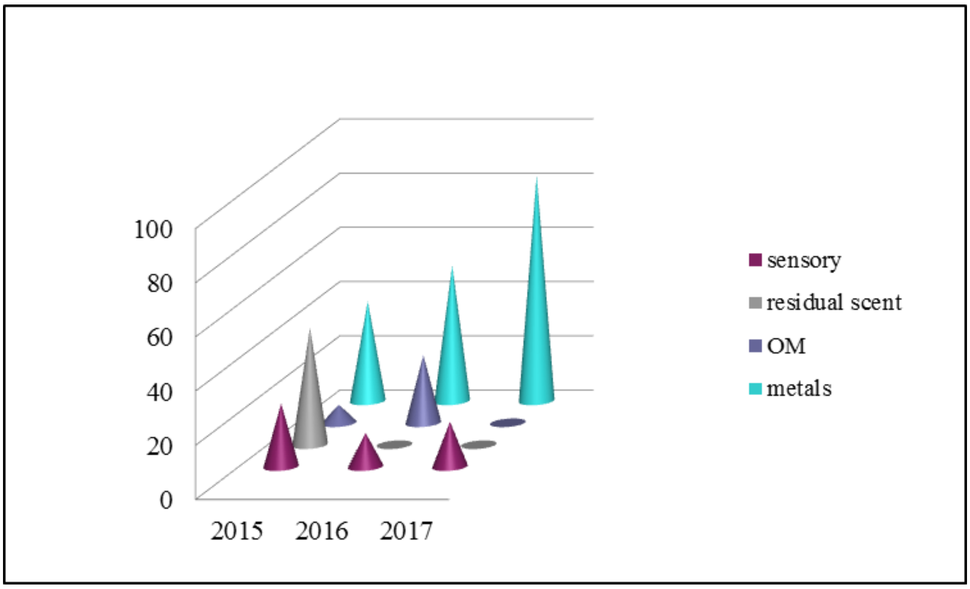

Figure 2 *Unsafety causes by years*

CONCLUSION

Based on results showed above we can make a conclusion that sensor characteristics change can affect specific migration increase of some of the contaminant sand that material is not stable. That presents the danger for packed foodstuff. Beside mentioned, the increase of total migration direct to unsafety and brings up the need for further analyses. Mentioned reasons should be considered while making a decision about analyses which means that controls should be deeper and more comprehensive and economically more accessible, as well.

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PHYSIOLOGICAL AND PATHOPHYSIOLOGICAL CHANGES ON BRAIN TISSUE RATS THROUGH THE OXIDATIVE STRESS PARAMETER

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Abstract

In this scientific research, the effect of toxic effects of heavy metals, cadmium was performed in vivo after acute intoxication of experimental animals of the albino Wistar rats and the protective effect of the S-donor ligand supplement, α-lipoic acid supplement. The parameters of the oxidative stress of alkaline and acid DNase in brain tissue were analyzed. The results of this study show physiological and pathophysiological changes when depositing cadmium in the brain tissue, which is observed by increasing the activity of DNase in the target organ. The α-lipoic acid that is given the day after each intoxication with heavy metal exhibits protective power to the brain tissue because it somewhat eliminates the toxic effect of heavy metals. This substance binds to itself cadmium by constructing a complex with it and acts as a powerful antioxidant agent. In reactions with free radicals, it reduces oxidative stress.

Keywords: Cadmium, α-lipoic acid, Brain, Oxidative stress

INTRODUCTION

According to the geochemical classification of chemical elements cadmium (Cd) is a lithophilic and halophilic element. Up to pH 8 is always present as a divalent positive ion (provided there are no phosphates and sulfates that can precipitate in the middle), when it can easily be sorbed on suspended particles or recombine complex compounds with organic ligands. Thus, with aquatic humic substances in the soil builds humane complexes. Through contaminated soils and water plants are the starting food link and the basic source of cadmium for animals and humans. The input of this metal with air is about 0.5 μg/day, while by water about 1 μg/day [1]. The concentration of cadmium in drinking water should be less than 1μg/l [2], and in soil less than 85 mg/kg. Cadmium affects the cycle of cell development, proliferation, differentiation, DNA replication and apoptosis.

α-lipoic acid (α-LA) is widely represented in foods of animal and plant origin, bound to proteins via lysine to lipolysin. Animal tissues rich in lipolysis are kidneys, heart and liver, while edible plants contain lipolysis spinach and broccoli. Small amounts of lipolysin were measured in tomato, peas and kale [3]. In the smaller percentage, its presence was also recorded in the plant-based intent (potatoes) [4]. This antioxidant reduces damage caused by radiation exposure, and can be used, in some instances, in the treatment of diabetes [5], as well as the prevention of complications of this (cardiomyopathy, neuropathy, and retinopathy) and other diseases.

MATERIALS AND METHODS

In this study, healthy albino laboratory rats of female sex, Wistar strain, 2-3 months old, body weight about 300 g were used. Animals are divided into 3 groups. In each group there were three animals. The control group is determined by the random selection method. The second group of laboratory animals received cadmium (II) chloride, and the third in addition to cadmium (II) chloride and α-lipoic acid. All experimental procedures and animal care in the vivarium of the Medical Faculty in Niš, Serbia, were carried out in accordance with the ethical principles of scientific research work on laboratory animals. The spectrophotometer Beckman DU 530 was used for the spectrophotometric determination of the oxidative stress parameter in the prepared brain tissue homogenate. The analysis of the activity of alkaline and acid DNase was performed [6,7].

STATISTICAL ANALYSIS

Statistical analysis of the results obtained during the test was done using Student's t-test for independent samples (Microsoft Office Excel). All results of the measurement are shown as the mean value ie. an arithmetic mean and the standard deviation (SD). The results of these analyzes are shown graphic (histogram).

RESULTS AND DISCUSSION

The toxic effect of heavy metals is that it stimulates the formation of free radicals and reactive oxygen derivatives in the organism, causing oxidative stress and leading to lipid peroxidation of the membrane thereby disrupting its functionality and selectivity in the transport of matter. In this way, cell damage, enzyme function or genetic material (DNA) can occur [8].

Acute potassium poisoning in laboratory animals leads to damage to the liver and testes, while chronic exposure leads to kidney damage, anemia, immune defects, and bone damage [9-11]. Chronic professional poisoning may occur after long-term exposure to cadmium by inhalation or oral route, and systematic exposure to cadmium exposure leads to increased calcium excretion, which is an increased risk of kidney stones and bone damage [12].

Although DNA is the most important biological target for the action of reactive oxygen radicals, not all types of radicals are equally toxic and do not act in a unique way. The superoxide anion is poorly reactive, while the hydroxyl radical is highly reactive [13-16]. DNA repair mechanisms are: direct reversion, reparation through cropping and recombination. Endonucleases are important in the crop of oxidatively modified thymine derivatives. This type of endonuclease is found in bacteria as type III endonuclease, and in mammals as γ-endonuclease.

Measurement of the value of protein in brain tissue

Calculating protein content in brain tissue is an important parameter in the process of measuring DNase activity (alkaline and acidic) because protein content is one of the indicators of DNase activity. According to the results obtained in this paper in the conditions of acute intoxication, Cd significantly changes the content of the same in the examined organ.

The level of these in the presence of supplements is somewhat normalized in relation to the control group, which is conditioned by the trend of change in the value of DNase. The results of calculating protein content in brain tissue homogenate after heavy metal intoxication (Cd) and administration of supplements (α-LA) are shown in Figure 1.

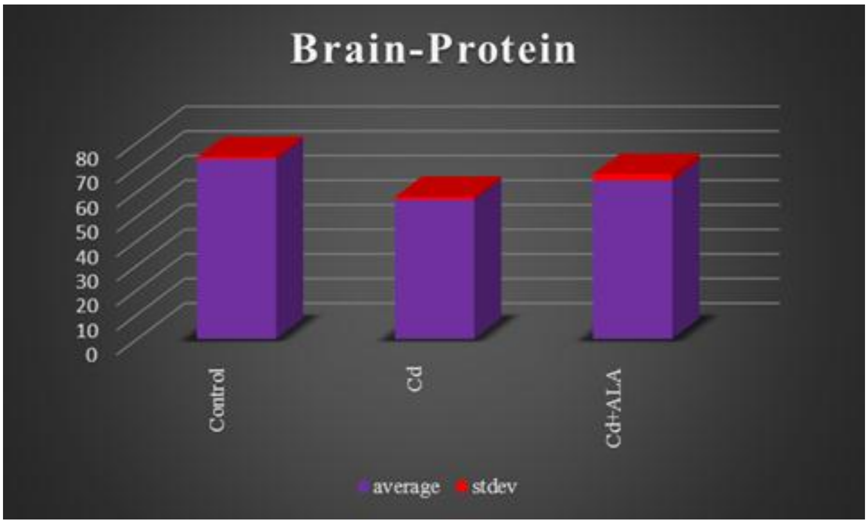

Figure 1 *Values of protein concentration in the brain*

Measurement of acid and alkaline DNase activity in brain tissue

From the results obtained in this study, it can be seen that cadmium significantly increases the level of alkaline DNase in the brain tissue (from 0.61 ± 0.08 to 1.35 ± 0.35). The acid DNase values after acute cadmium intoxication were increased in the brain (from 0.50 ± 0.03 to 1.55 ± 0.22) in relation to the control group of animals that were in the normal diet and life without cadmium inxication and without adding supplements. Exposure to cadmium cells includes not only the response of the signaling reaction to cell death but also the protective reaction of the cell against toxicity to this metal. Results of measurements of alkaline and acid DNase activity in brain tissue under conditions of acute intoxication of albino rats Wistar soybean ions Cd^{2+} as well as the effect of the supplement are shown on Figures 2 and 3.

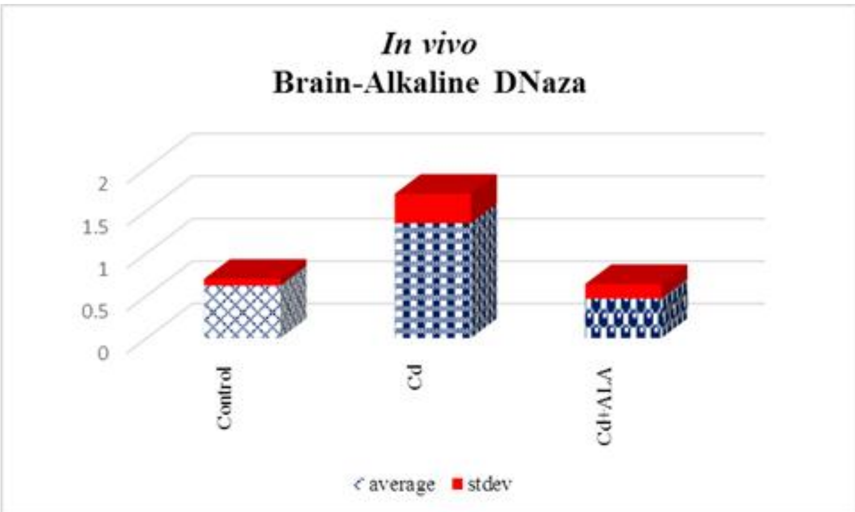

Figure 2 *Activity of alkaline DNase in brain tissue in experimental groups under conditions of acute cadmium intoxication and with the addition of an appropriate supplement*

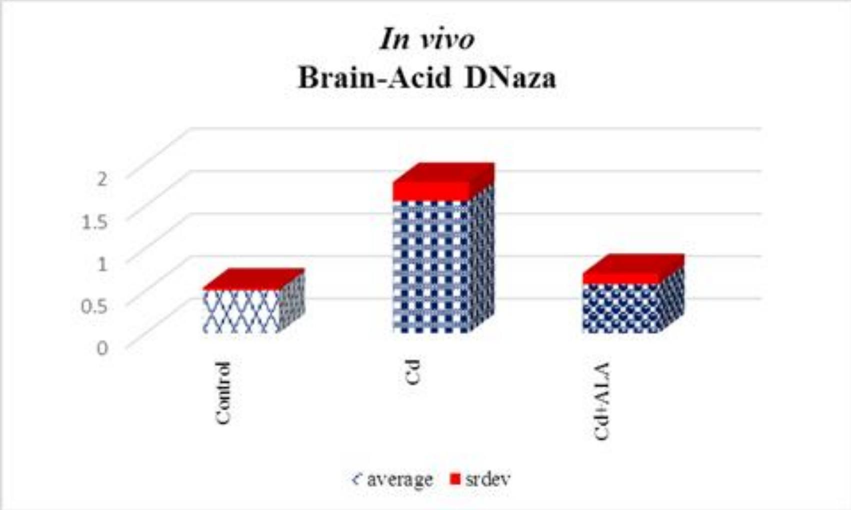

Figure 3 *Activity of acid DNase in brain tissue in experimental groups under conditions of acute intoxication cadmium and with the addition of an appropriate supplement*

According to the results in this study α-lipoic acid as a supplement significantly reduces the activity of DNase (alkaline and acid) brain (from 1.35 ± 0.35 to 0.46 ± 0.17 for alkaline DNase and 1.55 ± 0.22 to 0.57 ± 0.13 for an acidic DNase) in relation to the experimental group of animals which is cadmium-doped. By adding α-lipoic acid, one day after exposure to this metal during the duration of the experiment, about 70% reduces the effect of the toxic effects of the metal on the activity of acidic DNase. It is assumed that α-lipoic acid builds through -SH groups of poorly soluble mercaptides with a metal ion. However, the α-lipoic acid can also complex the ions of heavy metals [17]. Summarized on the basis of the results in this study α-LA exhibits a good protective effect in the brain tissue, which can be concluded by measuring the level of alkaline and acid DNase in the brain.

Proper nutrition rich in proteins, as well as various dietary supplements, e.g. α-lipoic acid suggest reduction and correction of the toxic effect of cadmium after its exposure. Also, the prevention of exposure to tobacco smoke, especially in children in the period of growth and development, can be an important factor of prevention when exposed to the effects of cadmium.

CONCLUSION

According to the results of the measurement of alkaline DNase activity of the brain, α-lipoic acid is a good supplement in acute cadmium poisoning by sublethal dose by intraperitoneal injection, based on the measurement of the activity of the alkaline DNase of the brain. According to the values of the acidic DNase activity, α- lipoic acid reduces the level of the same measured in cadmium-induced intoxication conditions and normalizes their value in the brain tissue.

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TOXICOLOGICAL AND PATHOPHYSIOLOGICAL MECHANISMS OF THE INFLUENCE OF LEAD AND α-LIPOIC ACID ON RAT BRAIN TISSUE

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Abstract

Lead can lead to increased formation of free oxygen radicals, so it can be talked about the genotoxic effect of this metal on the enzymatic and non-essential components of the antioxidant defense system of the organism. After the initiation of oxidative stress and consequent oxidative modification of the DNA molecule, the endonuclease, alkaline and acid DNase are involved, which participate in reparation of the damaged molecule in the examined organ. From the results obtained, it can be concluded that lead intoxication significantly changes the level of endonuclease. The assumption is that lead is a likely cause of oxidative damage to DNA, which is manifested by increased activity of alkaline and acidic DNase.

Keywords: Lead, α-lipoic acid, DNase, Protector

INTRODUCTION

Lead contamination sources are products of combustion in metallurgy and chemical industry, traffic, industrial wastewater and landfills. Professionally, lead workers are exposed to the lead in metal foundries and foundries of this metal, the paint industry, the ceramics and the glass manufacturing and processing industry, in the battery and battery industry, armaments and ammunition factories [1]. From the atmosphere, the soil, the water (surface and underground), lead (Pb) is introduced and retained in plants, and further down the food chain and drinking water goes into the human organism. The lead routes are very different. At a global level, until recently, most of the pollution of the atmosphere by lead was caused by the combustion of fuel in motor vehicles, where lead is present as an alkyl lead, a fuel additive [2]. In addition to this source, lead also comes from mining in mines, then recycling batteries and other materials containing lead. The maximum allowed concentration for lead (smoke and dust) is 0.15 mg/m^3 [3].

Leading this lead directly into the systemic circulation. It circulates mostly for erythrocytes, it is related to plasma albumin in the least part, and is least in ionic form or bound to low molecular weight proteins [4]. It is excreted from the body most of the urine, less through the mucous membrane of the digestive tract, through the lungs, hair, nails, sweat and milk. The "harmless" level of lead in the organism is still not defined [5].

The α-Lipoic Acid (α-LA), 6,8-dithioctanoic acid, was first isolated in 1951. by Reed *et al*. [6] as a catalytic agent known by different names and associated with pyruvate dehydrogenase. It is a cofactor of the multipurpose complex of pyruvate dehydrogenase and α-ketoglutarate dehydrogenase. It participates in the oxidative decarboxylation process of α-ketocyxin. Lipoic acid-thioxic acid is also referred to as the protogen and the acetate transfer factor.

The most important enzymes involved in DNA reparation are: DNA endonuclease, AP endonuclease, pyrimidine-hydrate-DNA glycosylase, DNA polymerase, β-lyase, δ-lyase, deoxyposodiodase, DNA ligase and others [7]. The superoxide anion is able to induce the synthesis of endonuclease IV. In reparation through the nucleotide excrement, exonuclease also takes a significant place, removing unwanted damaged DNA ends of the chain. DNase I is a glycosylated polypeptide that hydrolyzes one or both of the DNA strands [8]. In *in vivo* studies, the presence of DNase I has been shown to be very pronounced in the kidneys [9]. This enzyme is also considered a digestive enzyme, because it develops in the pancreas and parotid gland in the mammal, but also in the pituitary gland.

More than 50 years ago, DNase II or acid DNase was discovered, in addition to DNase I. At the cellular level, this enzyme is found in lysosomes with the basic function of degradation of exogenous DNA encountered during the process of phagocytosis and apoptosis of the cell [10,11]. It has also been confirmed that DNase II in acidic lysozyme can be found in necrosis states [12].

MATERIALS AND METHODS

In this study, healthy albino laboratory rats of female sex, Wistar strain, 2-3 months old, body weight about 300 g were used. All experiments were performed at the same time of the day to avoid circadian variations.

The control group is determined by the random selection method. The second group of laboratory animals received lead (II) acetate, and the third in addition to lead (II) acetate and α-lipoic acid. Subsequently, medial laparatomy, after sacrificing animals, homogenized the brain tissue with K Ultra Turrax IKA® T18 basic homogenizers in physiological solution as a medium. Then, analyzes of the determination of alkaline and acid DNase activity were performed [13].

STATISTICAL ANALYSIS

All results of the measurement are shown as the mean value ie. an arithmetic mean that represents a measure of central tendency and a measure of variability between data presented by standard deviation (SD) (Microsoft Office Excel). The results of these analyzes are shown graphic (histogram).

RESULTS AND DISCUSSION

Heavy metals can affect development and overall health causing depression, learning difficulties, neurological disorders, cardiovascular disease, liver disease, kidney disease, anemia, etc. Heavy metals are considered to be a continuous hazard as carcinogens for the human body [14].

As a metal with cumulative effect, lead is competitive with essential metals (iron, calcium, copper and zinc) for their numerous functions in the body, especially those related to the presence of free -SH groups in parts of proteins and enzymes of biomolecules. According to physical-chemical properties, Pb^{2+}-one can easily replace Ca^{2+}-one in calcified tissues (bones and teeth), but also in various soluble complexes of this metal with bioligands in biological fluids and tissues. Bone lead contributes to the development of osteoporosis, reduction of bone mass, changes in structure, and increased bone resorption in elderly people [15,16].

The active role of cadmium is reflected in the disorder of calcium metabolism leading to osteomalacia [17]. Unlike acute chronic intoxication, it leads to the development of some diseases, such as, for example, chronic obstructive pulmonary disease, kidney disease (nephrotoxicity), and bone (arthritis, osteoporosis), anemia, growth disorder, and others [18]. Excretion of cadmium from the organism is slow, and it occurs through the kidneys and biliary pathways, milk and saliva [19].

Internucleosomal DNA fragmentation, as a biochemical marker of apoptosis, is the decomposition of chromosomal DNA into oligonucleosis-like fragments [20]. There are deoxyribonucleases I (called DNase I ie alkaline DNase) and deoxyribonucleases II (DNase II, ie acidic DNase) [21-25].

Measurement of the value of protein in brain tissue

The level of protein can be a significant biochemical parameter that can be applied to the diagnosis and prognosis of many diseases. Reducing the concentration of proteins in the homogenate of the examined organ (brain) due to acute heavy-metal inoxication (Pb) indicates a negative nitrogen balance, while elevated values in the application of the (a-lipoic acid) supplements indicate a positive nitrogen balance and thus indicate the metabolic activity of the cell. The results of calculating protein content in brain tissue homogenate after heavy metal inoxication (Pb) and administration of supplements (α-LA) were shown by histogram in Figure 1.

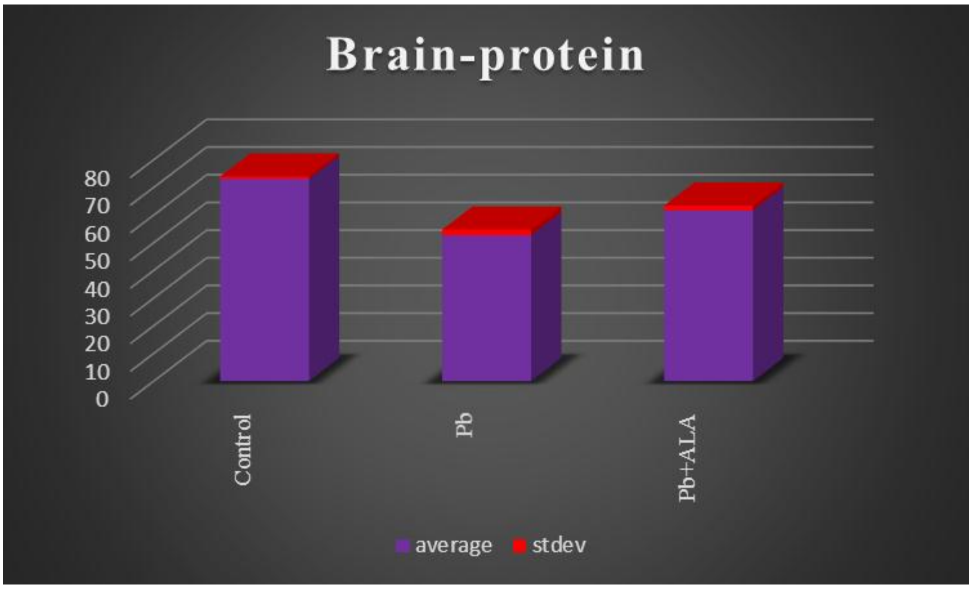

Figure 1 *Values of protein concentration in the brain*

Measurement of acid and alkaline DNase activity in brain tissue

From the results obtained in this study (Figures 2 and 3) it can be concluded that the effect of lead leads to an increased induction of oxidative stress in the brain tissue homogenate, which is manifested by a significant increase in DNase activity (from 0.62±0.08 to 1.6±0.23 for alkaline DNase and from 0.50±0.03 to 0.83±0.26 for acid DNase). It has also been observed that the antioxidative defense mechanisms in these animals are disturbed and they are present in the group of animals in the normal diet and without heavy metal intoxication.

When the cells exposed to the lead effect lead to DNA damage and an increase in the genotoxic effects in the cell, leading to the activation of DNAse that will participate in DNA reparation. By supplementing the supplements, the day after the exposure to the metal, during the duration of the to experiment, the effect of poisoning is reduced in part, and thus the enzyme activity (from 1.6±0.23 to 0.68±0.19 for alkaline DNase and from 0.83±0.26 to 0.61±0.35) in relation to the experimental group of animals which is cadmium-doped. α-LA as an effective antioxidant, the liposome and hydrosoluble compound easily passes through the membranes in the cytoplasm and participates in the protection against free reactive radicals.

The α-lipoic acid forms stable chelating complexes with Pb^{2+} and in this way acts as a good supplement and antioxidant in the fight against lead toxicity. α-LA may be a thiol-helator and a potential choice in treatment for lead poisoning. It is a preferred supplements due to the presence of -SH group which, via S-donor atoms, has the ability to complex with heavy metals, i.e. lead.

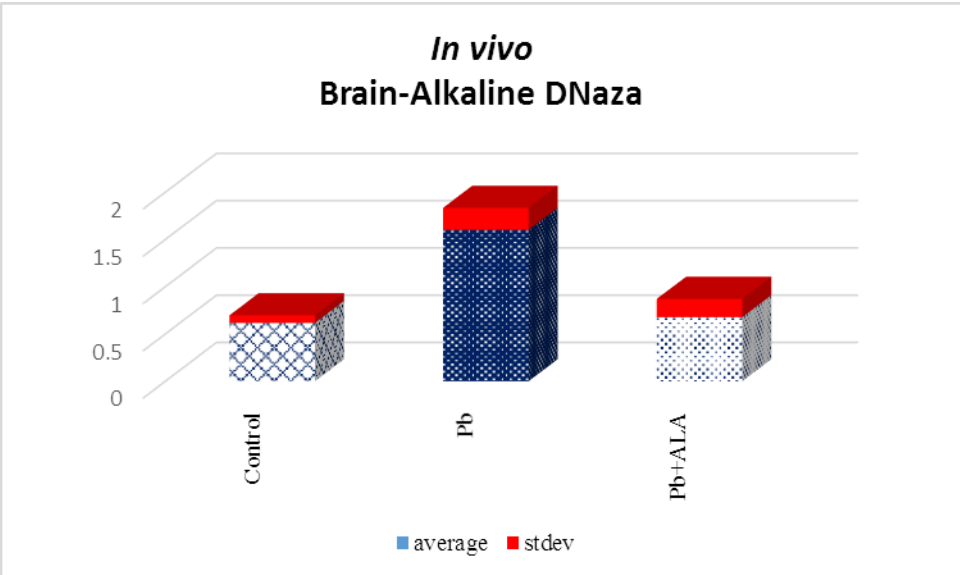

Figure 2 *Activity of alkaline DNase in brain tissue in experimental groups under conditions of chronic lead intoxication and with the addition of an appropriate supplement*

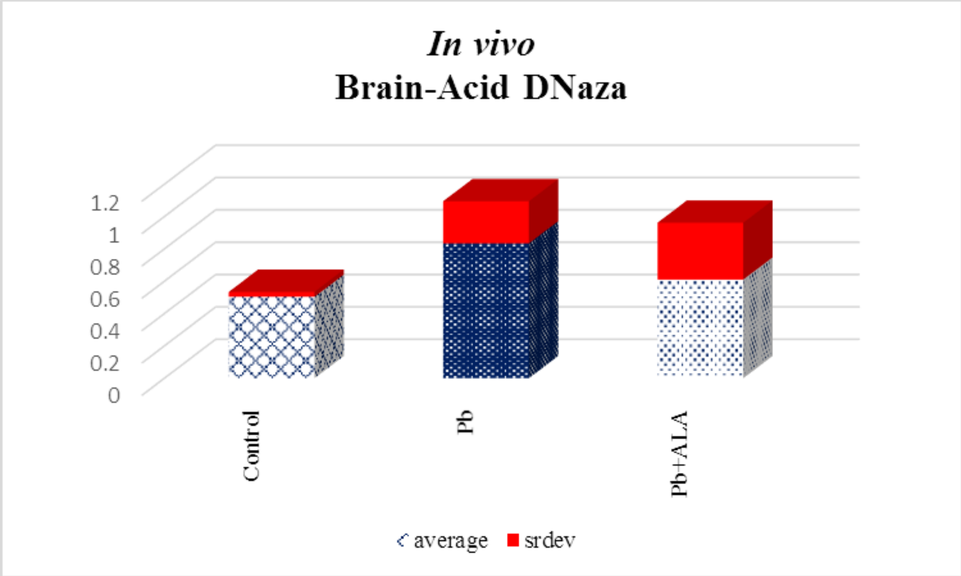

Figure 3 *Activity of acid DNase in brain tissue in experimental groups under conditions of chronic lead intoxication and with the addition of an appropriate supplement*

The therapy for the removal of heavy metals from the human organism is so called chelation therapy based on the coordination ability of metal ion on the one hand and the possession of a donor of the bioligand atom (-O, -N, -S) through which stable associations of the complex type are formed and thus significantly reduces their toxic effect.

CONCLUSION

Antioxidant α-lipoic acidas a powerful helator is necessary in the detoxification of reactive oxygen species in rats exposed to lead poisoning. It is a preferred supplements due to the presence of the -SH group which has the ability to complex with heavy metal through the S-donor atoms. Thus, the presence of this supplement, α-lipoic acid in nutrition is of great importance for the normal development of life processes in the cell.

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BIOCHEMICAL AND PATHOPHYSIOLOGICAL EFFECTS OF COPPER AND THE PROTECTIVE ROLE OF GLUTATHIONE IN WISTAR RATS

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Abstract

The model system for examining the influence of copper on hematological parameters was the study on albino rats of Wistar strain. In vivo research was performed after chronic intoxication of experimental animals with copper and the addition of glutathione supplements. The following haematological parameters were analyzed: erythrocytes, hemoglobin and hematocrit from the blood of the abdominal aorta. Under conditions of chronic copper toxicity, significant changes in haematological parameters have been observed: a slight decrease in the number of erythrocytes and a decrease in the percentage of hematocrit. However, the hemoglobin concentration is increased, which is explained by the mechanism for copper to participate in the synthesis of hemoglobin by assisting the installation of iron in the hem. Supplementation of glutathione, the day after the introduction of copper, leads to a decrease in the negative effect of this metal on hematologic parameters.

Keywords: Copper, Glutathione, Hematological parameters

INTRODUCTION

Copper particles are released into the atmosphere in the form of dust through volcanic eruptions, anthropogenic sources (pesticides, herbicides and fungicides) or from copper smelters and ore processing facilities. Copper compounds are used as bactericides, insecticides, algicides and fungicides, while copper (II) sulfate is used as a foam activator in the flotation of sulphide ores, in the production of azo colors, in the refining of petroleum and galvanoplastics [1]. Copper (Cu) is used for the construction of dental prosthetics, as well as some products in cosmetics.

As a result of increased human activity, the amount of copper in air, soil and water has also increased. The adult man's body contains 100-150 mg of copper, in large quantities it becomes toxic to the body. The concentration of copper in the serum of healthy people amounts to 11-20 μmol/L. Almost the total amount of copper in the body is protein-related, so the concentration of free copper ions is very small, unless there are some other disorders in the body. It is believed that as much as 35% of the population does not enter enough copper in the diet. The recommended daily intake of copper is about 2 mg [2]. This metal plays an important role in the process of erythropoiesis, bone mineralization, hemoglobin biosynthesis catalysis, a cofactor and a necessary element for the catalytic activity of numerous enzymes [3-5].

Copper is needed for the formation of red blood cells, enters the composition of hemocyanin, has a positive effect on the cell membrane of the nerve cells, and has an influence in the transmission of nerve impulses. The copper is necessary for the synthesis of phospholipids of the cell membrane and thus maintains a myelin that separates the nerve cells from the environment and regulates the level of the neurotransmitter. Copper also affects the healthy functioning of small blood vessels that control the flow of blood, nutrients and waste materials. It also affects the normal functioning of the blood vessels and is involved in the coating of blood vessels [6]. Copper is like a cofactor, an integral part of the enzyme spill and lysyl hydroxylase, an enzyme involved in the synthesis of collagen and the formation of connective tissue. Melanin production involves enzymes containing copper. The histaminease enzyme that metabolizes amino acid histamine requires copper for its functioning. The copper is also involved in the metabolism of fat and cholesterol, as well as the normal functioning of insulin, the synthesis of prostaglandin [7].

Blood is a fluid-binding tissue of an organism consisting of plasma and shaped elements: red blood cells, white blood cells and blood platelets.

Erythrocyte is a cell without core, biconical, discoidal appearance, a diameter of about 7.8 μm, and a thickness of about 2.4 μm peripherally, or 1 μm or less in the central part of the cell. Erythrocyte contains a very concentrated hemoglobin (Hb) solution, and hemoglobin accounts for 95% of the dry residue of erythrocyte. Although there is no core, mitochondria, and ribosomes, the erythrocyte is a highly specialized cell, which lives for 120 days and during that time it passes into the bloodstream about 300 kilometers, bringing all oxygen (O_2) tissues [8]. Erythrocyte is a very working dynamic unit. In the bone marrow, pluripotent haematopoietic stem cells from which all blood cells stimulate. Different peripheral blood cells are produced by successive divisions of pluripotent cells. These cells are reproduced throughout their lives and a small number remains the same as the stem cell. The predetermined stem cell producing erythrocytes is indicated by the abbreviation CFU-E (colony-forming unit-erythrocyte). Bone marrow normally produces about 900 trillion erythrocytes per hour and thus replaces the same number of erythrocytes that are simultaneously broken down by mononuclear macrophages of the histioconucleotide system. Normal erythrocyte lives 100-120 days. The number of erythrocytes in healthy subjects ranges between 4.2 and 5.8 million in μL in males, and between 3.7 and 5.2 million in μL in females [9].

MATERIAL AND METHODS

The model system for examining the effects of copper exposure is a study on white rats of Wistar soybean, female sex, 6 weeks old, weighing 230±30 g. Experimental animals were grown in laboratory conditions in a normal diet in the vivarium of the Medical Faculty in Nis, in accordance with the rules of the Local Ethics Committee. The control group is determined by the random selection method. The second group of laboratory animals was inoculated with copper(II)-sulfate, and the third in addition to copper(II)-sulfate also received glutathione (GSH). All procedures were performed after anesthesia of rats with ketal (35 mg/kg body weight) in accordance with the principles of sacrifice in laboratories. Blood samples were obtained from the abdominal aorta with a heparinized syringe for the determination of hematologic parameters.

Determination of hematological parameters

Haematological parameters of erythrocytes (RBC), hemoglobin (Hb) and hematocrit (Hct) were determined on the automatic analyzer at the Clinic for Nephrology, the Clinical Center in Niš, according to the procedure that is used in biochemical laboratories.

STATISTICAL ANALYSIS

All measurement results are shown as the mean ± SD. The student's t-test for independent samples (Microsoft Office Excel) was applied for the statistic processing of results. The results of these analyzes are tabulated and graphically (histogram).

RESULTS AND DISCUSSION

Hemoglobin is the most important hemoprotein in the human organism that is in red blood cells. Hemoglobin is a deep tetramer consisting of two pairs of identical polypeptide chains, and each polypeptide chain contains a prosthetic group in the hem. Hem is a complex of porphyrin and iron ferro-iron (II). Porphyrin located in hemoglobin is protoporphyrin IX. The role of hemoglobin is to transfer oxygen from the lungs to its capillaries, from which hemoglobin passes into the cells in which it is used in the breathing processes. The erythrocytes do not have the ability to synthesize proteins, so they do not have the ability to replace any protein or component of the erythrocyte membrane that is damaged and becomes dysfunctional. It is of the almost importance for the erythrocyte to have the ability to prevent or repair the damaged essential molecules such as hemoglobin or membrane lipids and proteins. Two serious sequelae of hemoglobin oxidation: the created methemoglobin is not capable of bonding the oxygen and the superoxide-anion radical, which was created in this process. It is also highly reactive and can oxidize many biological molecules, especially membrane lipids.

The results of measurements of the values of standard hematological parameters (RBC, Hb and Hct), as well as changes in the conditions of chronic copper inoxication and the effect of glutathione supplements are shown in Table 1.

Table 1 *The values of the haematological parameters of the experimental group of animals after chronic intoxication copper and the effect of the supplement (GSH) day after exposure to copper*

Chematological parameters	Control	Cu	Cu + GSH
RBC [$\times 10^{12}$/L]	7.48 ± 0.18	7.09 ± 0.09	7.47 ± 0.25
Hb [g/L]	141.67 ± 0.58	152.67 ± 9.71	163.33 ± 4.04
Hct [%]	40.17 ± 2.10	35.23 ± 0.91	36.9 ± 1.61

Exposure to copper leads to a slight decrease in the number of erythrocytes in the blood, from 7.48 ± 0.18$\times 10^{12}$/L for the control group of animals up to 7.09 ± 0.09$\times 10^{12}$/L for the group of animals receiving copper. The blood Hb level significantly increases relative to the group that was in the normal lifestyle and diet (from 141.67 ± 0.58g/L to 152.67 ± 9.71g/L), probably because copper is necessary for the synthesis of hemoglobin which helps to install Fe in the hem and catalyzes the porphyrin biosynthesis and reticulocyte maturation. In a word, this heavy metal is necessary for hematopoiesis. In our study it was confirmed that copper catalyzes Hb biosynthesis by increasing Hb content by about 8% and this effect in the presence of GSH, more pronounced. While the percentage of hematocrit decreases in a group of experimental animals chronically intoxicated with copper compared to the experimental group that was in the normal diet and lifestyle (from 40.17 ± 2.10% to 35.23 ± 0.91%).

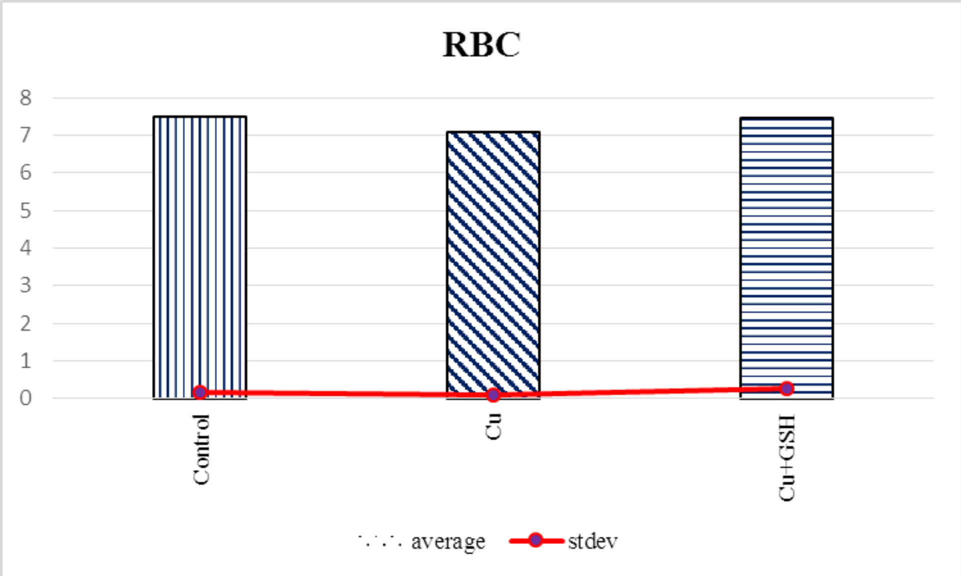

Figure 1 *The trend of changes in typical haematological parameter (RBC) after chronic copper toxication with or without supplement (GSH)*

It has been shown in this study that glutathione dosed as supplements in copper coping has a favorable effect on hemoglobin content in the blood. The number of erythrocytes and the percentage of hematocrit slightly decreased in this experimental group of animals compared to the control group. Through its active sites -SH GSH added as a supplement after metallic (copper) intoxication allows the binding of metals and the construction of complexes with them [10]. GSH is a powerful thiol chelate anti-poisoning agent (especially copper) with which it forms a stable complex, relieves the harmful effect of metals on erythrocytes and thus exhibits its antioxidant effect [11,12]. Erythrocytes represent a good model system for the antioxidant effect of gluatination against the oxidative stress of all biological cell membranes.

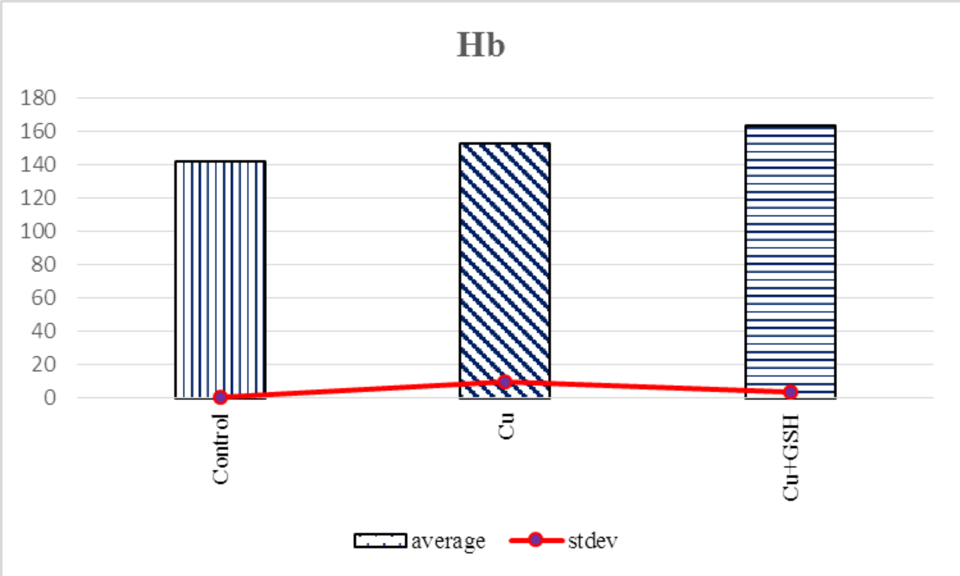

Figure 2 *The trend of the change in the typical hematological parameter (Hb) after chronic intoxication copper with and without protrusion (GSH)*

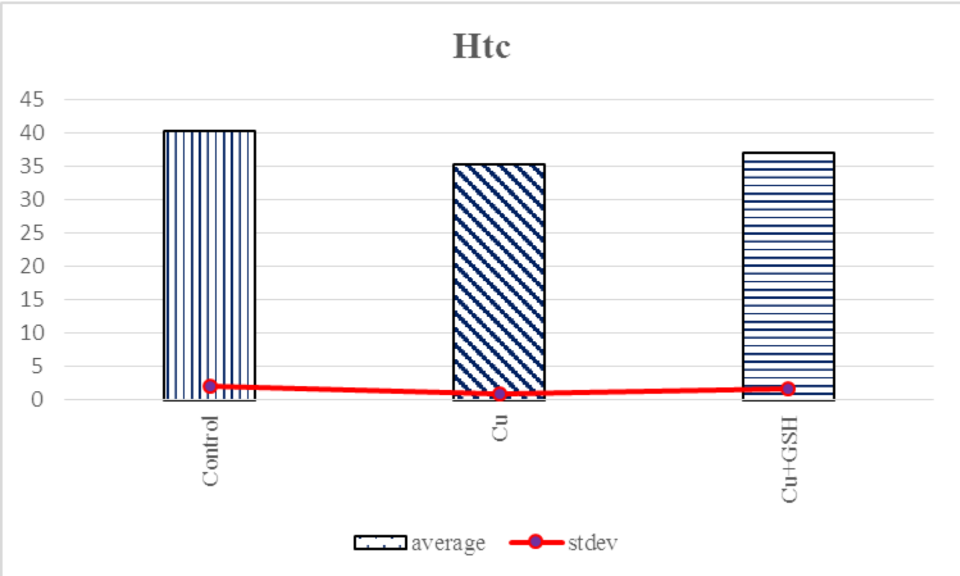

Figure 3 *The trend of the change in the typical hematological parameter (Hct) after chronic intoxication copper with and without protrusion (GSH)*

Copper is an essential element for normal erythropoiesis, as observed by Hart *et al.* [13], which proved that the diet of whole milk, supplemented with iron in the rat, causes an anemia that is cured by the addition of copper in food. The lack of copper in the body can lead to anemia, because it causes poor iron absorption and reduces the number of erythrocytes, then osteoporosis, neurological disorders, psychosis, cardiac disorders, reduces the amount of leukocytes and the organism's resistance to disease, as well as a number of other disorders. Symptoms of deficiency are: changed heart rhythm, hair loss, feeling of weakness of the organism and others.

CONCLUSION

Under conditions of chronic copper toxicity, significant changes in the value of haematological parameters occur: a slight decrease in the number of erythrocytes, increased hemoglobin concentration (because copper participates in the synthesis of hemoglobin by helping to incorporate iron into the hem), the percentage of hematocrit is reduced. Addition of supplement (GSH), on the day after copper smothering, eliminates the negative effect of metal (Cu) that manifests itself in hematological parameters (RBC and Hct).

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ELECTROCHEMICAL BEHAVIOR OF PARACETAMOL IN ALKALINE SOLUTION AT PLATINUM ELECTRODE

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Abstract

Paracetamol/acetaminophen/APAP is commonly used analgesic. Hence, it is expected to be found in the environment and it brings out the question of its monitoring. One of the possible ways for it might be the application of some electroanalytical technique. Electrochemical behavior of paracetamol is studied in sodium tetraborate solution using platinum electrode. Methods applied are cyclic voltammetry and square-wave voltammetry. The results suggest that these methods can be applied for the detection of paracetamol and determination of its concentration in the sample. These methods are also very easy to perform and results are obtained in a very short time, which make them very convenient.

Keywords: Paracetamol, Platinum electrode, Sodium tetraborate, Cyclic voltammetry, Square-wave voltammetry

INTRODUCTION

Paracetamol/acetaminophen/APAP, structure presented in Figure 1, is very commonly used analgesic. Hence, it is expected to be found in the environment. This is proven by Morasch *et al.* [1] who studied the presence of micropollutants, among which are some pharmaceutical compounds like paracetamol, in the Vidy Bay of Lake Geneva, Switzerland. They also investigated their concentrations in water from waste water treatment plant and their removal between treatment plant and lake water which is also used as the reservoir of drinking water. Nevertheless, they found that the paracetamol concentrations exceeded predicted no-effect concentrations in raw drinking water samples and therefore present a potential risk to the ecosystem. The results like these bring out the question of monitoring of pharmaceutical compounds such as paracetamol in water systems. The application of some electroanalytical techniques can be one of the possible ways to do that.

Electrochemical behavior of paracetamol was studied using different kinds of electrochemical systems and different methods. For example Engin *et al.* [2] used glassy carbon electrode for voltammetric determination of paracetamol, whereas Feizbakhsh *et al.* [3] studied electrocatalytic oxidation of paracetamol on glassy carbon electrode modified with Ni or NiCu. Pedrosa *et al.* [4] studied the possibility of application of flow injection analysis method for determination of paracetamol using gold electrode modified with 3-mercaptopropionic acid. Sanghavi and Srivastava [5] used carbon nanotube paste electrode modified with Triton X 100 for simultaneous determination of paracetamol, aspirin and caffeine by adsorptive stripping differential pulse voltammetry. Various media was used for the studies of electrochemical behavior of pharmaceutical compounds such as 0.1 M NaOH

[3,6], 0.5 M H_2SO_4 [2], phosphate buffer [2,4-6], acetate buffer [2], Britton Robinson buffer [2] and 0.1 M $NaClO_4$ [8].

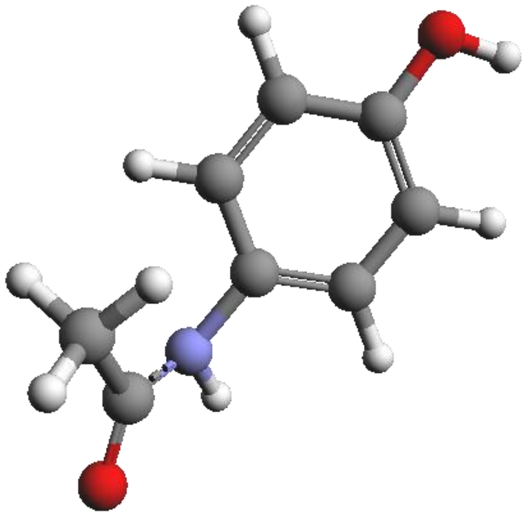

Figure 1 *Structure of paracetamol*

In this study, electrochemical behavior of paracetamol is investigated in sodium tetraborate solution using platinum electrode. Methods applied are cyclic voltammetry and square-wave voltammetry. These methods are also very easy to perform and results are obtained in a very short time that makes them very convenient. The experimental results suggest that these methods can be applied for the detection of paracetamol and determination of its concentration in the sample.

MATERIALS AND METHODS

Potentiostat (IVIUM XRE, IVIUM Technologies) with the appropriate software was used for electrochemical testing. The system was made up of three electrodes. The working electrode was platinum electrode. The reference electrode was saturated calomel electrode (SCE) and platinum electrode was used as the auxiliary. Applied methods were cyclic voltammetry, as well as square-wave voltammetry.

Cyclic voltammetry was performed in the presence of $7.94 \cdot 10^{-5}$ M paracetamol between potentials -1.000 and +1.000 V vs. SCE at various scan rates: 10 mV/s, 100 mV/s, 200 mV/s and 1000mV/s. Besides that, various amounts of paracetamol ($3.17 \cdot 10^{-5}$ M, $7.94 \cdot 10^{-5}$ M, $1.11 \cdot 10^{-4}$ M, $1.59 \cdot 10^{-4}$ M) were added to the solution and cyclic voltammetry was performed at scan rate of 200 mV/s to see the effect of paracetamol concentration on current density.

Square-wave voltammetry parameters were: potential range 0.0 – 0.8 V vs. SCE, E step 4 mV, pulse amplitude 25 mV, frequency 15 Hz.

Paracetamol was obtained from the pharmacy as a commercial product in the form of oral suspension. Supporting electrolyte was 0.1 M $Na_2B_4O_7$. All measurements were conducted at room temperature (298K) in naturally aerated solutions. The potential is expressed referring to a saturated calomel electrode (SCE).

RESULTS AND DISCUSSION

Cyclic voltammetry

Cyclic voltammetry measurements are conducted in two different ways in order to inspect the effect of scan rate and concentration on the shape of voltammogram and on the recorded current density value. Figure 2 presents cyclic voltammograms recorded at different scan rates in the range of 10 - 1000mV/s in the presence of the same concentration of paracetamol, $7.94 \cdot 10^{-5}$ M.

It can be seen that peak current increases with scan rate increase, peak potential is around 400 mV vs SCE at scan rate 10 mV/s and shifts towards more positive values as the scan rate increases. Similar value is observed by other authors [6,9].

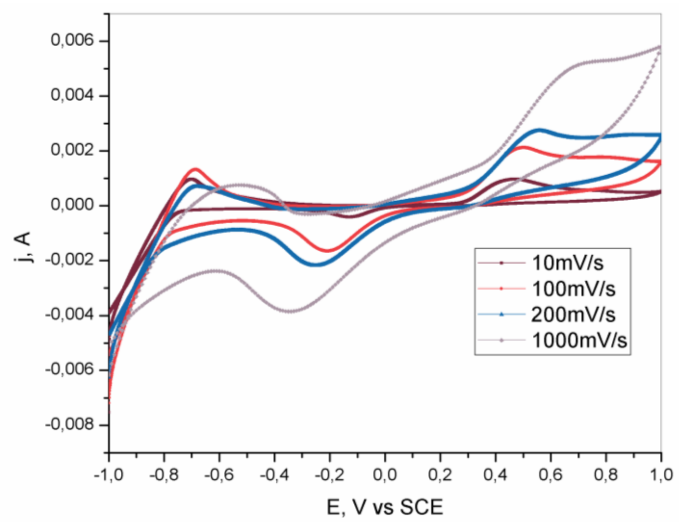

Figure 2 *Cyclic voltammograms recorded on Pt in the presence of $7.94 \cdot 10^{-5}$ M paracetamol at various scan rates*

In Figure 3a correlation between peak current and square root of scan rate is presented and the fact that the correlation is linear indicates that the electrode reaction is controlled by diffusion [3,10].

Plot of log j_p vs log v, Figure 3b, where fitting gives linear correlation, allows the appropriate equations to be derived:

$\log j_{pa}/\mathrm{mA} = 0.36391 \log v/\mathrm{mVs}^{-1} - 0.39035$ ($R^2 = 0.99776$)

$\log j_{pc}/\mathrm{mA} = 0.4937 \log v/\mathrm{mVs}^{-1} - 0.83818$ ($R^2 = 0.97223$)

indicating predominant diffusion control of both anodic and cathodic processes [2,8]. Diffusive character of current peak is important since in that case it can be used for determination of the studied compound [8].

a) *b)*

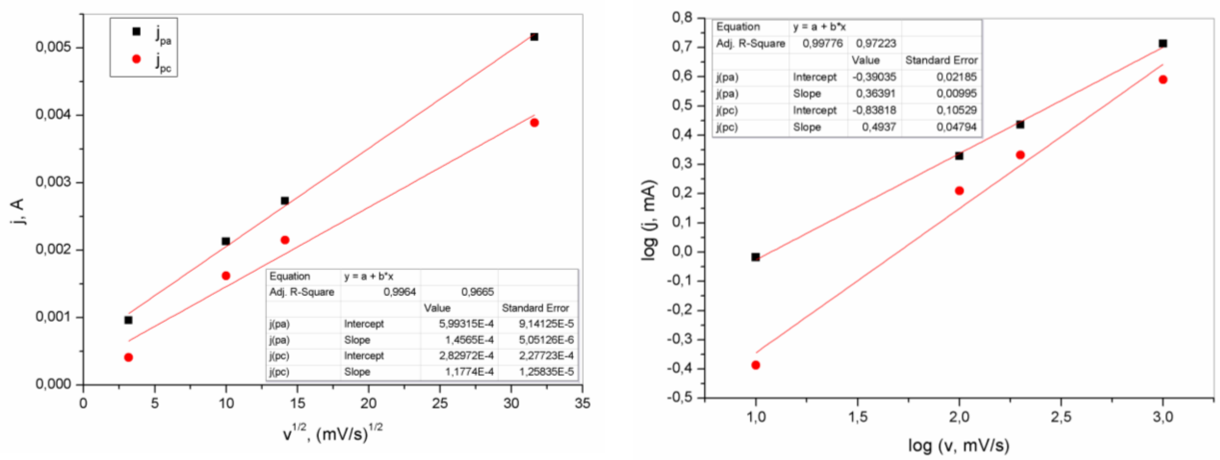

Figure 3 *a) Plot of square root of scan rate versus peak current, b) plot of logarithm of peak current versus logarithm of scan rate recorded in cyclic voltammogram on Pt in 0.1 M $Na_2B_4O_7$ in the presence of $7.94\cdot10^{-5}$ M paracetamol*

The effect of different concentrations of paracetamol on electrochemical behavior is also studied and the results are presented in Figure 4. It can be seen from voltammograms that anodic peak current increases regularly with the paracetamol concentration, Figure 4a. Linear correlation can be observed in Figure 4b and the appropriate equation is:

$$j_{pa}/A = 21.95279\ c/\text{moldm}^{-3} + 6.85948\cdot10^{-4}\ (R^2 = 0.92161)$$

The R^2 value for correlation between cathodic current peak and paracetamol concentration is far from 1 so it can't be used for determination of paracetamol content under tested conditions.

a) *b)*

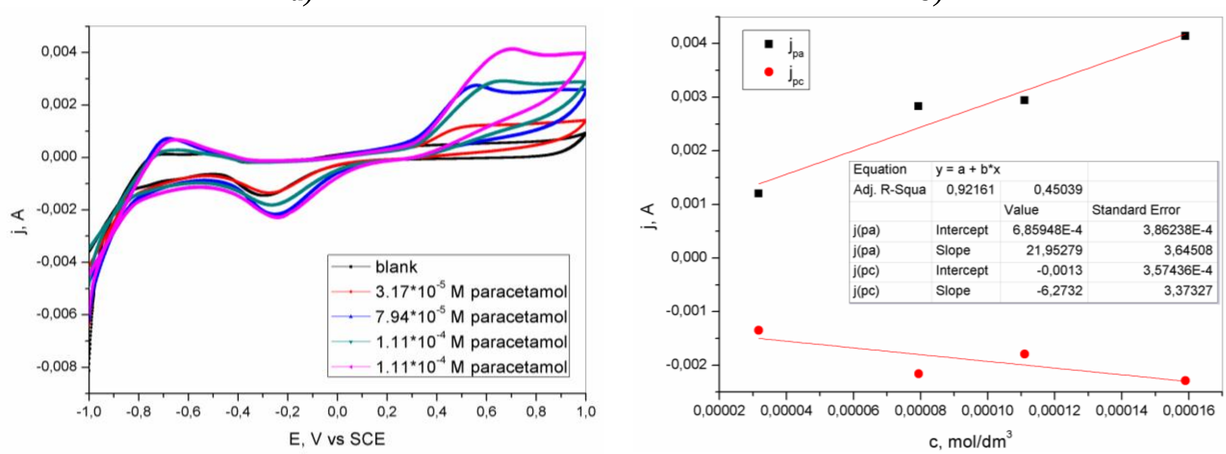

Figure 4 *a) Cyclic voltammograms recorded on Pt in the presence of $3.17\cdot10^{-5}$ M, $7.94\cdot10^{-5}$ M, $1.11\cdot10^{-4}$ M and $1.59\cdot10^{-4}$ M paracetamol at a scan rate of 200 mV/s, b) plot of paracetamol concentration versus peak current*

Square-wave voltammetry

Square-wave voltammetry (SWV) is proven to be very effective analytical technique [6,11]. It can be performed rapidly and can be very sensitive. Square-wave voltammograms recorded in 0.1 M $Na_2B_4O_7$ on Pt in the presence of $3.17\cdot10^{-5}$ M, $7.94\cdot10^{-5}$ M, $1.11\cdot10^{-4}$ M,

$1.59\cdot10^{-4}$ M paracetamol are presented in Figure 5a. It can be seen that peak current increases with paracetamol concentration whereas linear correlation between those two parameters is presented in Figure 5b, and the corresponding equation is j_p/A = 1.82611 c/moldm^{-3} + $2.98267\cdot10^{-4}$ (R^2 = 0.9449). It can be concluded that SWV is adequate technique for determination of paracetamol amount in tested solution. Similar behavior is described by Doulache *et al.* [6].

a) *b)*

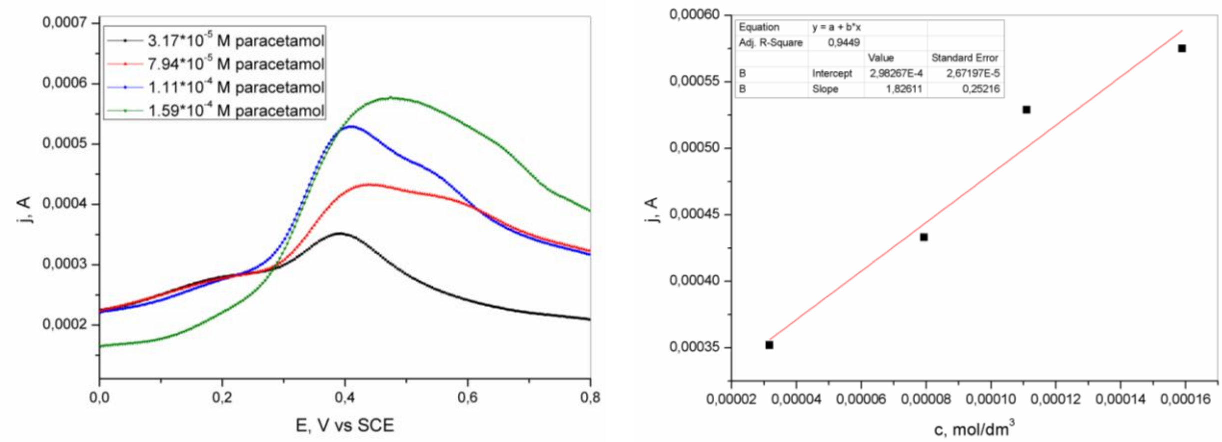

Figure 5 *a) Square-wave voltammograms for paracetamol in 0.1 M sodium tetraborate on Pt with f=15 Hz, a=25 mV, ΔE_s=4 mV, and concentration in the interval $3.17\cdot10^{-5}$ M - $1.59\cdot10^{-4}$ M , b) plot of paracetamol concentration versus peak current*

According to the observed experimental behavior and several literature sources [2,6,9,11] the electrooxidation mechanism of paracetamol in $Na_2B_4O_7$ aqueous solution on Pt electrode can be proposed, Figure 6.

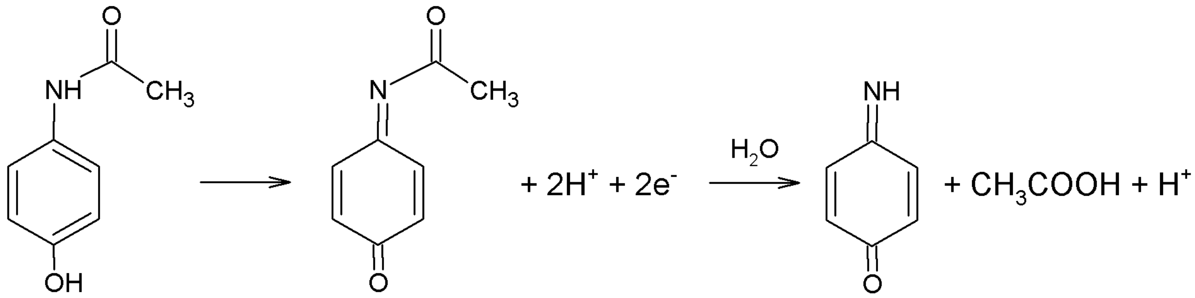

Figure 6 *Oxidation mechanism of paracetamol [2,6,9,11]*

CONCLUSION

Electrochemical behavior of paracetamol in alkaline solution of 0.1 M $Na_2B_4O_7$ at platinum electrode is studied, using cyclic voltammetry and square-wave voltammetry.

The effects of changes of scan rate and paracetamol concentration are observed by comparison of cyclic voltammograms recorded under different experimental conditions and it can be concluded that the increase of scan rate or paracetamol concentration leads to anodic peak current increase. The electrooxidation process is under diffusion control so it is possible to use these data for determination of paracetamol amount in the system. These conclusions are confirmed by square-wave voltammetry results.

The linear correlation between the anodic peak current, found in voltammogram either cyclic or square-wave, and paracetamol concentration that is expressed by the appropriate equation can be used to analyze the paracetamol content.

ACKNOWLEDGEMENT

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ELECTROANALYTICAL INVESTIGATION AND DETERMINATION OF IBUPROFEN

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Abstract

The subject of this paper is determination of ibuprofen in sample using cyclic voltammetry method. This pharmaceutical compound is one of the most used analgesic drugs and accordingly its residuals contaminated the environment. So it is important to find a sufficiently sensitive method for its determination. Electrochemical oxidation and reduction of ibuprofen (2-(p-isobuthylphenyl) propionic acid) was studied in 0.1 M Na_2SO_4 solution as supporting electrolyte. The dependence of the current peak on scan rate and concentration was investigated. In accordance with the obtained results, it is concluded that the proposed electroanalytical method may be applied for determination of ibuprofen.

Keywords: Ibuprofen, Pharmaceutical compound, Platinum electrode, Cyclic voltammetry

INTRODUCTION

Ibuprofen (2-(p-isobuthylphenyl) propionic acid) is an anti-inflammatory, analgesic and antipyretic drug. Having that in mind, it is largely used in treatment of muscle and head pain, inflammation in rheumatic disease and also for treatment of fever [1]. Due to frequent use of ibuprofen in various pharmaceutical forms, its residuals contaminate environment [2]. According to the literature [3], residuals of ibuprofen are detected in water. Actually, the large use of pharmaceutical compounds classifies them as micro pollutants in surface waters [4]. As a consequence, it is important to determine ibuprofen and for that purpose different methods including spectrophotometry [5], chromatography [6], and capillary electrophoresis [7] are used. However, these methods are not sensitive enough and nowadays researchers are using electroanalytical techniques. The cyclic voltammetry as one of the electroanalytical methods is characterized by high sensitivity, selectivity, simplicity and short time analysis in regard to the other techniques and have proven to be useful for the determination of organic molecules including drugs [8]. Different electrode materials were used for electrochemical oxidation and reduction processes of ibuprofen including boron-doped diamond (BDD) electrode [9], Ti/TiO_2-RuO_2 and Ti/IrO_2-RuO_2 [10,11]. According to Montes *et al*. [12] a proposed mechanism of ibuprofen oxidation involves single-electron transfer via radical cation formation followed by decarboxylation. The structural formula of this pharmaceutical compound is presented in Figure 1.

The aim of this paper is to examine electrochemical behaviour of ibuprofen on platinum electrode using cyclic voltammetry technique and 0.1 M Na_2SO_4 solution as supporting electrolyte.

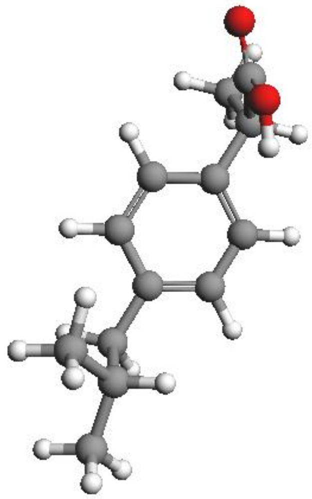

Figure 1 *Structure of ibuprofen*

MATERIALS AND METHODS

Electrochemical measurements

Electrochemical measurements were performed by potentiostat (IVIUM XRE, IVIUM Technologies) with appropriate software. Three-electrode system containing the platinum electrode as working electrode, standard calomel electrode as the reference and platinum wire as the auxiliary electrode was used. Cyclic voltammetry was performed in this investigation in a potential range from -1 V (vs SCE) to 1 V (vs SCE) with various scan rates (10 mV s^{-1}, 100 mV s^{-1}, 200 mV s^{-1}, 1000 mV s^{-1}). The investigated concentration of ibuprofen was $9.7\cdot10^{-4}$ M, $2.4\cdot10^{-3}$ M, $3.4\cdot10^{-3}$ M, $4.8\cdot10^{-3}$ M, $7.3\cdot10^{-3}$ M, $9.7\cdot10^{-3}$ M and cyclic voltammetry was carried out at scan rate of 200 mV s^{-1}. The effect of scan rate on the electrochemical oxidation of ibuprofen was also examined at concentration of $2.4\cdot10^{-3}$ M. Ibuprofen was purchased in pharmacy. Supporting electrolyte was 0.1 M Na_2SO_4 and all experiments were performed at an ambient temperature.

RESULTS AND DISCUSSION

Cyclic voltammetry

The cyclic voltammetry is used to investigate the electrochemical oxidation and reduction of ibuprofen at platinum electrode in 0.1 M Na_2SO_4 solution. The obtained cyclic voltammogram is illustrated in Figure 2. According to this figure, the anodic peak at around -0.50 V (vs SCE) implies to oxidation of ibuprofen.

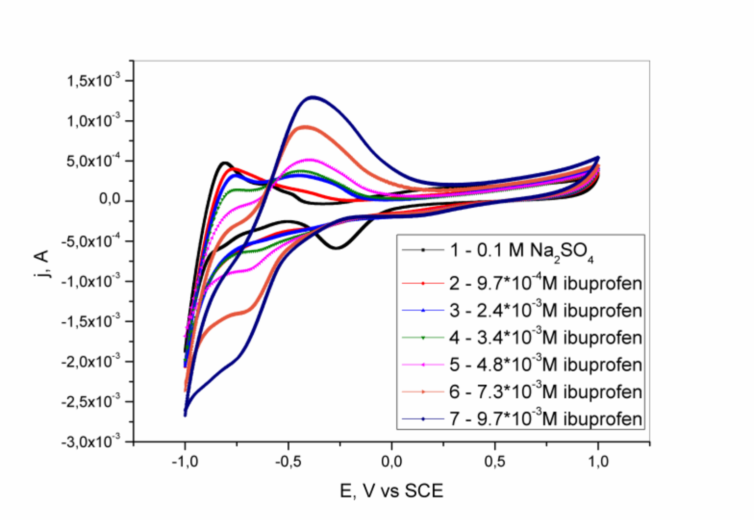

Figure 2 *Cyclic voltammetry obtained on Pt electrode in the presence of different concentration of ibuprofen at scan rate of 200 mV s^{-1}*

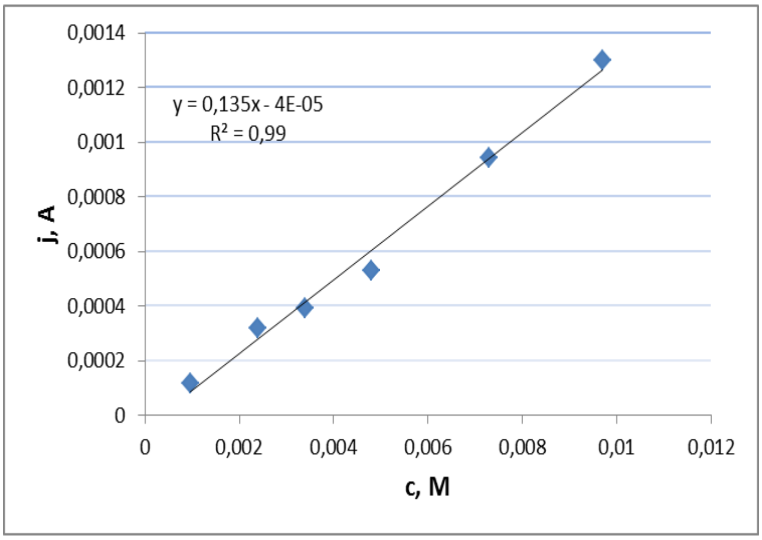

Figure 3 *Plot of ibuprofen concentration versus peak current*

It is known that the peak current depends on the concentration of investigated compound. Accordingly, Figure 3 illustrates the dependence of peak current on ibuprofen concentration and it is observed that there is linear correlation between them.

The electrochemical behaviour of ibuprofen (for $2.4 \cdot 10^{-3}$ M) at various scan rates was also examined by cyclic voltammetry. Thus, it will be determined whether the adsorptive or diffusive character of anodic peak dominates [13]. As can be seen in Figure 4, the peak current increases with increasing scan rates. Because current is the ratio of charge to time, a faster scan rate gives larger peak current.

Figure 5 illustrates linear correlation between the peak currents (Ip) and the square root of the scan rate ($\nu^{1/2}$) and the equation can be shown as:

$$I_p(A) = 1 \cdot 10^{-5} \nu (mV \cdot s^{-1}) + 0.0001; \quad R^2 = 0.9153 \qquad (1)$$

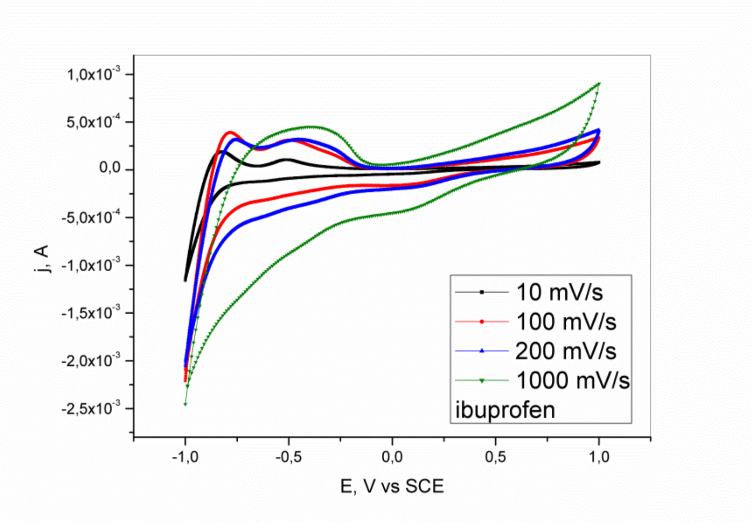

Figure 4 *Cyclic voltammograms recorded on Pt in the presence of 2.4·10^{-3} M ibuprofen at different scan rates*

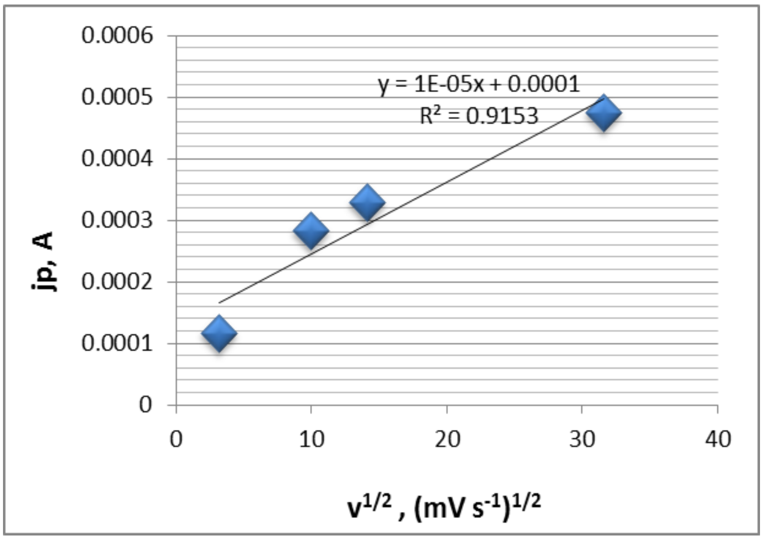

Figure 5 *Plot of square root of scan rate versus peak current recorded by cyclic voltammetry on Pt in 0.1 M Na_2SO_4 in the presence of 2.4·10^{-3} M ibuprofen*

In addition, with increasing the scan rate, the oxidation peak slightly shifted toward more positive potentials, suggesting a kinetic limitation in the reaction of ibuprofen at a surface of platinum electrode (Figure 6) [13] and the equation can be shown as:

$$E_p(V) = 0.0651 \log \nu (mV \cdot s^{-1}) - 0.58; \quad R^2 = 0.9831 \qquad (2)$$

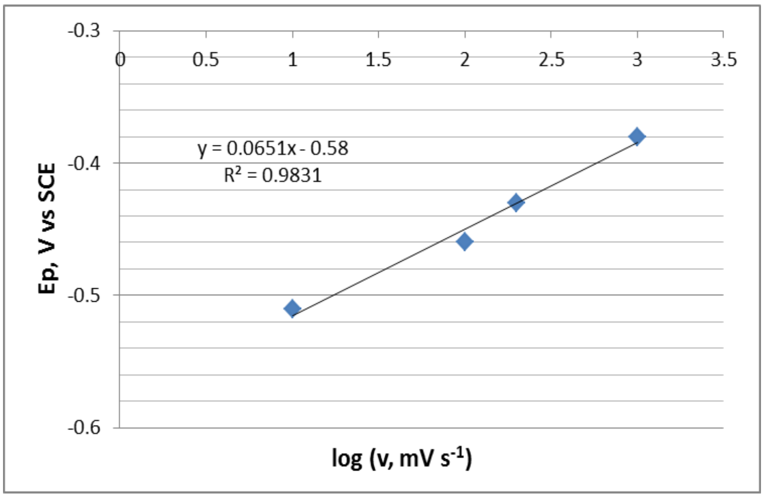

Figure 6 *Plot of peak potential versus logarithm of scan rate recorded by cyclic voltammetry on Pt in 0.1 M Na_2SO_4 in the presence of $2.4 \cdot 10^{-3}$ M ibuprofen*

A plot of logarithm of the anodic peak current versus logarithm of the scan rate showed a straight line with slope of 0.31. According to the relevant literature [1,14-16] if the slope is close to 1 it is about adsorptive character while the slope value close to 0.5 indicates the diffusion-controlled process. According to the Figure 7, the obtained value of slope points to diffusion character of electrochemical oxidation of ibuprofen. Similar results were obtained by Suresh *et al*. [17].

$$\log I_p(A) = 0.3122 \log v (mV \cdot s^{-1}) - 4.228; \; R^2 = 0.9778 \qquad (3)$$

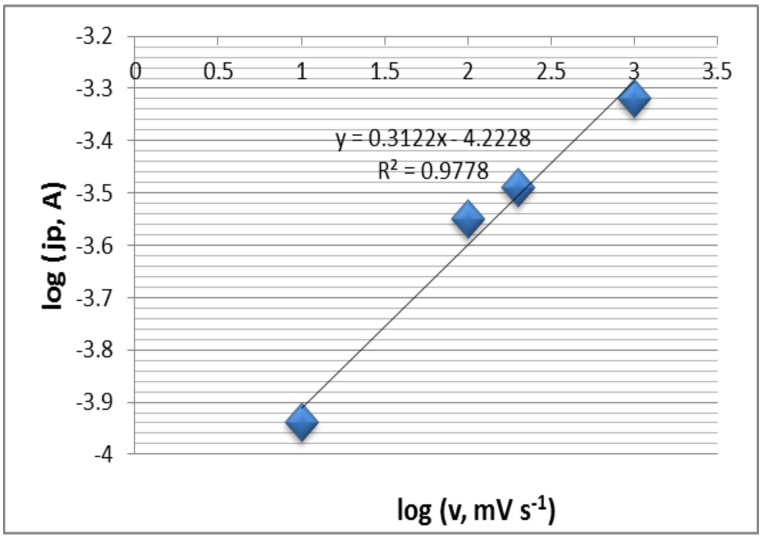

Figure 7 *Plot of logarithm of peak current versus logarithm of scan rate recorded by cyclic voltammetry on Pt in 0.1 M Na_2SO_4 in the presence of $2.4 \cdot 10^{-3}$ M ibuprofen*

Also, the linear relationship of the peak current and scan rate (Figure 7) indicates that the electrode reaction is surface-controlled process [18,19].

CONCLUSION

The cyclic voltammetry method provides a simple and quick tool for the direct determination of ibuprofen in neutral sulphate solution using platinum electrode. The linear correlation between logarithm of scan rates and logarithm of peak current indicated that the electrochemical oxidation is under diffusion control. Besides, it is noted that with the increase of scan rate and concentration of ibuprofen, the peak current also increases. Therefore, the cyclic voltammetry, as one of the electroanalytical method, may be considered as an appropriate alternative to the others such as chromatographic methods.

ACKNOWLEDGEMENT

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CORROSION BEHAVIOR OF STEEL IN RINGER'S SOLUTION IN THE PRESENCE OF AMOXICILIN

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Abstract

This paper deals with examination of the behavior of amoxicilin (Ospamox) as a corrosion inhibitor of steel in Ringer's solution at pH 6. Electrochemical techniques such as open circuit potential measurements, linear voltammetry and cyclic voltammetry were used for that purpose. Potentiodynamic polarization measurements show that amoxicillin acts as a cathodic type of inhibitor in Ringer's solution. Adsorption of amoxicillin in Ringer solution obeys Langmuir adsorption isotherm. Also, Gibbs free energy of adsorption has a value -28.2 kJ/mol and indicates spontaneous and strong adsorption of inhibitor molecule on the electrode surface.

Keywords: Corrosion, Ringer's solution, Steel, Ospamox, Amoxicilin

INTRODUCTION

Ideally, implants should be completely inert in the human body, but unfortunately this is a very rare case [1]. They encounter different biological environments, different physico-chemical properties, and their interaction with tissues and bones is very complex problem [2]. They come in contact with body fluids, such as blood and fluids which contain water, sodium, chlorine, proteins, and amino acids [3]. Stainless steels are Fe-based alloys that contain at least 12% Cr, which is necessary for the formation of a passive film on their surface. Stainless steels are divided into several classes, depending on the chemical composition and structure. Increased content of Cr and presence of other elements (Ni, Mo, N, etc.) leads to high corrosion resistance of steel in various environments [4].Besides that, many investigators try to find way to decrease dissolution of metal and alloys using different organic compounds.However, most of them are toxic and hazardous for the environment. Extensive investigations are carried out to find efficient corrosion inhibitors which are biodegradable and non-toxic for the environment. During recent years, it was noted that different drugs can effectively protect metals from attack of aggressive ions [5].One of them is amoxicillin (Ospamox) which is a semisynthetic aminopenicillin i.e. an antibiotic with bactericidal activity.

MATERIALS AND METHODS

In this investigation three electrode cell system was used. Working electrode was electrode made of stainless steel 316L, saturated calomel electrode (SCE) was the reference electrode and the platinum was auxiliary electrode. Electrochemical measurements were performed by potentiostat (IVIUM XRe, IVIUM Technologies) with appropriate software. Prior to each measurement, the electrode was polished with grinding paper and alumina (0.3μm Al_2O_3), washed with distilled water and dried in the air. Substances used during the work are: NaCl (VWR Prolabo, Belgium), KCl (ZorkaŠabac), $CaCl_2$ (Alkaloid Skopje) for the preparation of the Ringer's solution and amoxicillin (Ospamox) (Sandoz GmbH, Austria) as a potential inhibitor. Amoxicillin was used in wide range of concentration ($1 \cdot 10^{-4}$ M - $7 \cdot 10^{-3}$ M).The methods used during the test were: open circuit potential measurement (OCP), linear voltammetry and cyclic voltammetry. The open circuit potential was determined over 30 minutes. Then, the polarization curves were plotted from the value of the open circuit potential to -0.9 V vs. SCE in the cathode direction and up to 0.5 V vs. SCE in the anodic direction. Cyclic voltammetry was recorded in wider range from -0.8 V vs. SCE to 1.0 V vs. SCE. Scan rate was 1 mV/s for potentiodynamic polarization measurements and 10mV/s for cyclic voltammetry measurements. All measurements were carried out at room temperature and in naturally aerated solutions.

RESULTS AND DISCUSSION

Open circuit potential measurements were done for 30 min in Ringer's solution with and without the presence of different concentrations of the amoxicillin. The obtained average values for OCP are shown in Figure 1.

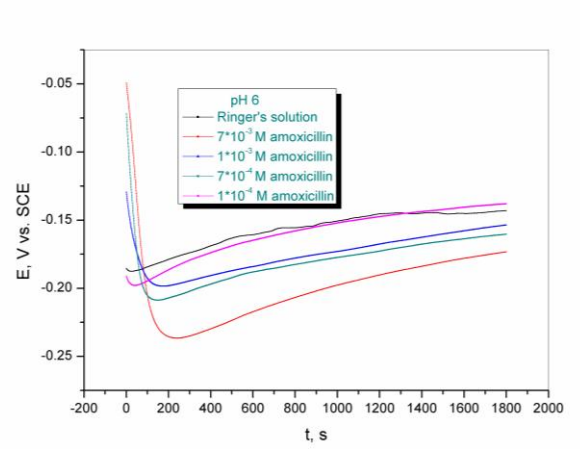
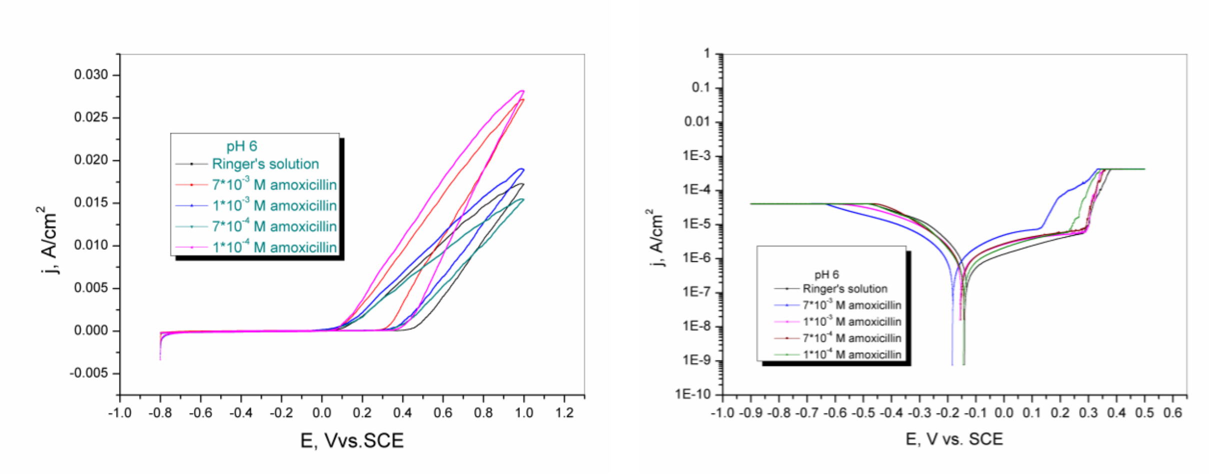


Figure1 *The open circuit potential of stainless steel 316L in Ringer's solution without and with the addition of various amount of amoxicilin*

In the Ringer's solution with the addition of the inhibitor value of OCP becomes more negative which is probably associated with the adsorption of the inhibitor molecules on the steel surface [6, 7]. Based on the change in value of the open circuit potential in the presence of the inhibitor, it can be expected that amoxicillin acts as mixed-type inhibitor in examined circumstances and that will be discussed later. Figure 2 shows cyclic voltammetry and polarization curves of 316L steel in Ringer's solution in the presence of various amount of inhibitor.



a) b)

Figure 2 *Cyclic voltammetry curves (a) and potentiodynamic polarization curves (b) for stainless steel 316L in Ringer's solution without and with addition of different concentration of amoxicilin*

From Figure 2a it can be seen that at potential of 0.38 V comes to a sudden increase of current density indicating a more intense oxidation of steel. The sudden increase of the current density is probablythe result of dissolution of protective layer formed on the surface of the electrode. Passivation of steel in saline solutions is based on the formation of a layer that consists mostly of chromium and iron oxides.Nickel and molybdenum oxides are also an integral part of the passive layer but in a smaller amount. Efficiency of the protective layer depends on the film thickness, adhesion of the inhibitor molecule on the surface of the metal and the diffusion of oxygen and metal ions in the oxide [8].

In case of corrosion of steel or iron, electrochemical reactions can be written in the following order [9]:

Anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

When iron corrodes, the corrosion rate is controlled by cathodic reactions. Cathodic reactions which occur during steel corrosion in neutral solution are:

Evolution of hydrogen:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2)$$

Reduction of oxygen:

$$O_2 + 4H_2O + 4e^- \rightarrow 4OH^- \qquad (3)$$

Reduction of metal ions:

$$M^{3+} + e^- \rightarrow M^{2+} \qquad (4)$$

Metal deposition:

$$M^+ + e^- \rightarrow M \qquad (5)$$

Small amount of carbon in steel contributes to stability of steel in chloride solutions. Also, presence of molybdenum increases the resistance of steel to corrosion. Besides that, chromium allows the formation of a passive layer in the form of chromium oxide on the steel surface [10]. Due to the different dissociation, Cr_2O_3, iron oxide and nickel oxide cannot remain in balance. Chromium oxidizes and reduces oxides of iron or nickel by the following reactions [11]:

$$Fe_2O_3 + 2Cr = Cr_2O_3 + 2Fe \quad (6)$$

$$3Fe_3O_4 + 8Cr = 4Cr_2O_3 + 9Fe \quad (7)$$

$$3NiO + 2Cr = Cr_2O_3 + 3Ni \quad (8)$$

MoO_2 can be formed on steel surface and protect metal from further corrosion. However, increase of the potential leads to increase of current density due to transpassive oxidation of Mo^{4+} to Mo^{6+} [12]:

$$Mo + 2H_2O \rightarrow MoO_2 + 4H^+ + 4e^- \quad (9)$$

$$MoO_2 + 2H_2O \rightarrow MoO_4^{2-} + 4H^+ + 2e^- \quad (10)$$

Linear potentiodynamic measurements are often used to evaluate the corrosion of metal alloys [12]. Figure 2b shows the polarization curves of steel 316L in Ringer's solution with and without addition of the inhibitor.

On the basis of the polarization curves, it can be seen that the corrosion potential is shifted to more negative values with increase of concentration of inhibitor. Also, based on the polarization curves, it can be seen that cathodic current density decreases with an increase of concentration of the inhibitor indicating that in Ringer’s solution amoxicillin acts as cathodic type of inhibitor.

Electrochemical parameters of stainless steel 316L in Ringer’s solution with and without the addition of various amount of amoxicillin were calculated on the basis of potentiodynamic curves and obtained values for corrosion potential (E_{corr}), corrosion current density (j_{corr}), cathodic (b_c) and anodic (b_a) Tafel slopes are shown in Table 1. Values of inhibition efficiency (IE) and degree of coverage (θ) are also presented in Table 1 in addition to the electrochemical parameters.

***Table 1** Electrochemical parameters of steel in Ringer's solution with and without the addition of the inhibitor*

Solution	E_{corr}(V vs. SCE)	j_{corr}(A/cm^2)	bc (mV/dec)	ba (mV/dec)	θ	IE (%)
Ringer’s solution	-0.130	$3.021 \cdot 10^{-6}$	-0.267	0.735	/	/
$7\cdot10^{-3}$ M amoxicillin	-0.181	$1.508 \cdot 10^{-7}$	-0.014	0.019	0.9503	95.03
$1\cdot10^{-3}$ M amoxicillin	-0.153	$3.550 \cdot 10^{-7}$	-0.032	0.073	0.8824	88.24
$7\cdot10^{-4}$ M amoxicillin	-0.147	$4.614 \cdot 10^{-7}$	-0.067	0.129	0.8474	84.74
$1\cdot10^{-4}$ M amoxicillin	-0.141	$5.58 \cdot 10^{-7}$	-0.114	0.216	0.8162	81.62

From Table 1 it can be seen that the degree of coverage depends on the concentration of the inhibitor. Degree of coverage increases with increase of concentration of the amoxicillin. At lower concentrations of the inhibitor, the degree of coverage is lower, which is probably the result of the transition of MoO_2oxide which affects the stability of the protective film. Also, it can be seen from the Table 1 that the corrosion potential in the presence of the inhibitor is shifted to more negative values, which suggests that amoxicillinaffects cathodic corrosion processes [13].

The mechanism of adsorption of inhibitoron the steel surface was investigated using the Langmuiradsorption isotherm. The adsorption of the inhibitors on the metal surface is the most important step in the inhibition mechanism. Langmuir adsorption isotherm of amoxicillin on the steel is shown in Figure 3.

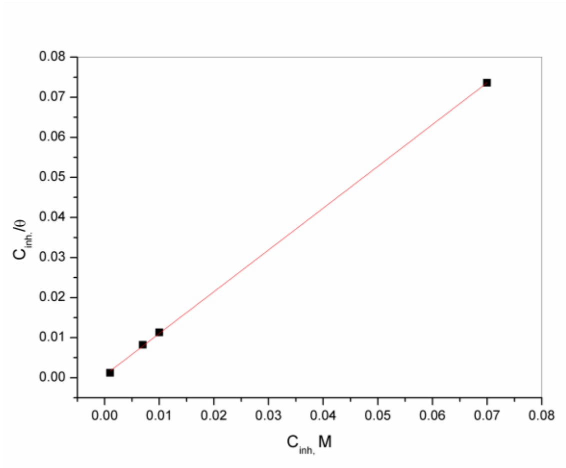


***Figure 3** Langmuir adsorption isotherm of amoxicillin on the stainless steel 316 L surface*

Gibbs free energy of adsorption has a value of -28.2 kJ/mol and indicates strong and spontaneous adsorption of amoxicillin on the steel surface.

CONCLUSION

Amoxicillin shows good inhibition efficiency against 316L steel corrosion in Ringer's solution. Presence of inhibitor in chloride solution leads to adsorption of molecules of amoxicillin on the steel surface. Potentiodynamic measurements have shown that amoxicillin in Ringer's solution acts as cathodic type of inhibitor. Adsorption of amoxicillin on stainless steel surface obeys Langmuir adsorption isotherm.

ACKNOWLEDGEMENTS

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ADSORPTION BEHAVIOUR OF Cu^{2+} ONTO ORIGINAL AND MODIFIED ELECTRIC ARC FURNACE SLAG

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Abstract

Electric arc furnace slag (EAFS) and alkali activated slag (AAS) prepared by alkali activation of EAFS have been used as new adsorbent for Cu^{2+} removal from wastewaters. The adsorption experiments have been carried in a batch conditions in the pH and initial concentrations ranges of 3-5 and 50-150 mg L^{-1}, respectively. The results have shown that highest adsorption capacities were obtained at pH of 5 and initial concentration of 100 mg L^{-1}. Moreover, alkali activation of EAFS enhance the Cu^{2+} adsorption. Adsorption by both adsorbents occur via chemisorption.

Keywords: Steel slag, Copper, Alkali activation, Adsorption

INTRODUCTION

Discharge a wastewater into environment without pre-treatment may present the serious risk for inland water and soil. Thus, a special attention is paid to the wastewaters treatment before being discharged into environment and currently, adsorption is considering as an effective method [1]. Metallurgical slag, the by-products from the sector of ferrous metallurgy, has been proposed as highly efficient adsorbents for the removal of heavy metals from wastewaters [2]. In this sense, electric arc furnace slag (EAFS), the by-product of steel production in electric arc furnaces, has gained the great interest [3-5]. EAFS is very complex system which primarily comprises of oxides of calcium, iron, silicon, aluminium and manganese and its chemical composition depend on operational conditions of furnace and the grade of steel purity. The mechanism of sorption of heavy metals on the slag surface is supposed to be ion-exchange of Ca^{2+} resulting in the metal cations binding on the slag surface by means of chemical bond [6] mainly in the form of hydrooxocomplexes [7].

The sorption properties of ferro metallurgical slags are limited by their physic-chemical characteristic. This slag is characterized by the low porosity and low specific surfaces which limit their sorption properties [8]. Thus, different method has been applied in order to improve the sorption properties of slag primarily by the modification of type and amount of surface groups and pore structure. The two-step dissolution coprecipitation modification procedure using HCl and NaOH was applied to produce the highly porous blast furnace slag with enhanced adsorption properties for removal of Cu^{2+} and phosphorous from wastewaters [9]. The removal of Ni^{2+}, PO_4^{3-} and NH_4^+ from wastewater can be improved by the thermal activation of steel making slag [10]. Acid treatment of slag and mixing of acid treated slag and $Al(OH)_3$ with subsequent heating of mixture [10] have also proved to improve the sorption properties of slag.

In this paper, the electric arc furnace slag modification by alkali activation known as alkali activated slag (AAS) was used for investigation of Cu^{2+} removal from wastewaters and the sorption properties of AAS and EAFS were compared.

MATERIALS AND METHODS

Materials

The powdered EAFS is used for the adsorption study. The main oxide constituents of EAFS were 46.5 % CaO, 23.5 % FeO, 12.2 % SiO_2, 6.5 % MgO, and 7.24 % Al_2O_3. The two types of adsorbent were used in this study: (1) the original slag material (EAFS) and (2) the slag modified by alkali activation (AAS). The procedure of AAS sample preparation and detailed characterisation are described previously [12]. The both samples, EAFS and AAS, were crushed, sieved to particle sizes below 63 µm, washed with deionized water until the pH of the wash water was kept 7 ±0.5 and dried at 105 °C.

The batch adsorption tests

The batch adsorption tests were performed by the mixing of solid EAFS and AAS samples with water containing the Cu^{2+} at solid to liquid ratio 0.4 for a period of 35 min at 20 ^oC. Solution of Cu^{2+} was prepared from analytical grade chemicals, copper sulphate ($CuSO_4 \times 5H_2O$,) in deionised water. The effect of pH and initial copper concentration on the removal of Cu^{2+} are investigated at a temperature of 20 ^oC. Three values of pH = 3, 4 and 5 and initial concentrations of Cu^{2+} ranging from 50 to 150 mg L^{-1} are applied in an adsorption tests.

The pH of solution was adjusted by the addition of H_2SO_4. After adsorptions tests, the solutions were filtered and concentrations of Cu^{2+} in filtrates were analysed via ICP-OES. The amount of Cu^{2+} uptake by adsorbents i.e. adsorption capacity q_t at any time t (mg g^{-1}) was determined following Eq. (1).

$$q_t = \frac{(C_o - C_t)}{m} V \tag{1}$$

where C_0 and C_t are the initial and final concentrations of Cu^{2+} (mg L^{-1}) in solution, V is the volume of Cu^{2+} ions solution (L), and m is the dry mass of adsorbent (g).

The adsorption kinetic was evaluated using the pseudo-first-order, pseudo-second-order models.

RESULTS AND DISCUSSION

The results of investigation of influence of pH of solution on the removal efficiency of Cu^{2+} from aquatic solution are given in the Figure 1a. The experiments were not carried out at the pH above 5 because the precipitation of coper hydroxide. It can be seen that adsorption capacity increases rapidly with the increase of pH from 3 to 4. Further increase of pH from 4 to 5 slowly increases of adsorption capacities of both adsorbents. The adsorption data obtained at different initial Cu^{2+} concentrations are shown in Figure 1b. The maximal adsorption capacities for both adsorbents were obtained at the initial Cu^{2+} concentrations of 100 mg L^{-1}. Furthermore, increase of initial concentrations lead to the decrease of adsorption capacity, thus the kinetic of Cu^{2+} removal from wastewaters was evaluated kipping the constant pH and initial Cu^{2+} concentrations of 5 and 100 mg L^{-1}, respectively.

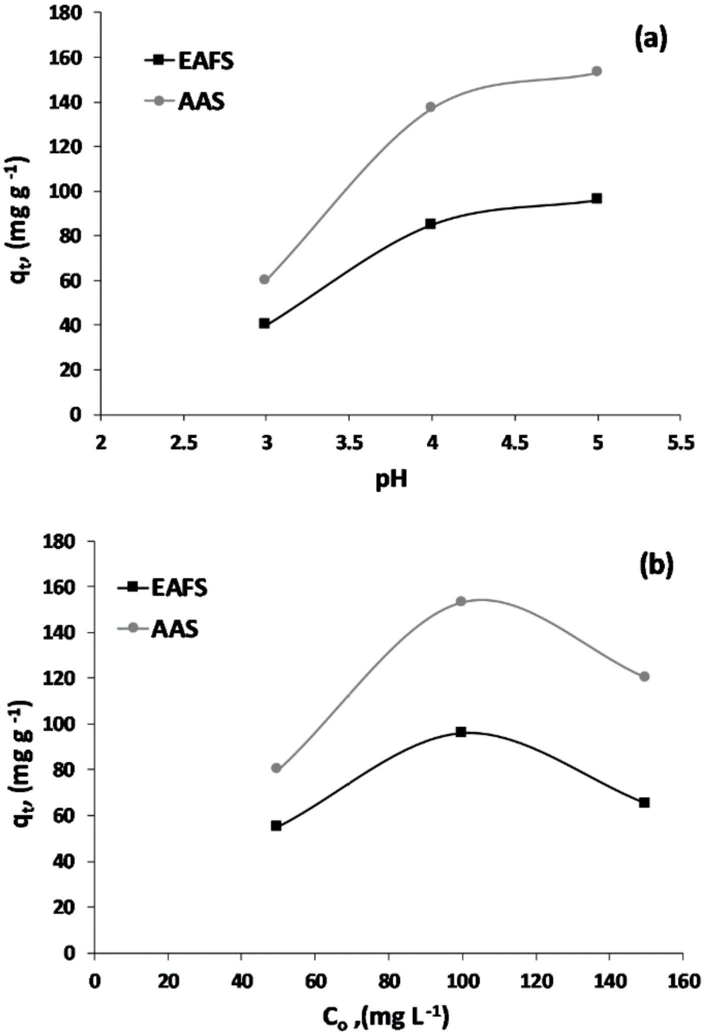


Figure 1 *Influence of pH (a) and initial concentration of Cu^{2+}(b) on the adsorption process*

Effect of contact time on the Cu^{2+} adsorption onto the EAFS and AAS were investigated in the range of 2-35 min. The results of adsorption studies indicate the improved adsorption of Cu^{2+} onto AAS in comparison to EAFS (Figure 2a). The achieved adsorption capacities within 35 min of adsorption process at 20 ^oC were 96 and 153 mg L^{-1} for EAFS and AAS sorbent, respectively. Moreover, the uptake of Cu^{2+} ions from aquatic solution by the EAFS and AAS is very rapid in initial stage of adsorption due to the presence of number of available active sites. The major fraction of Cu^{2+} was adsorbed onto the EAFS within the first 5 min. The prolongation of adsorption processes up to 15 min slowly increases the metal uptake and afterward practically has no influence on the removal efficiency. This indicates that adsorption of Cu^{2+} onto EAFS reaches equilibrium within 15 min. In the case when AAS was used as sorbent, the removal efficiency of Cu^{2+} was also rapid in a first 5 min, but thereafter increases slowly up to 25 min when equilibrium was reached.

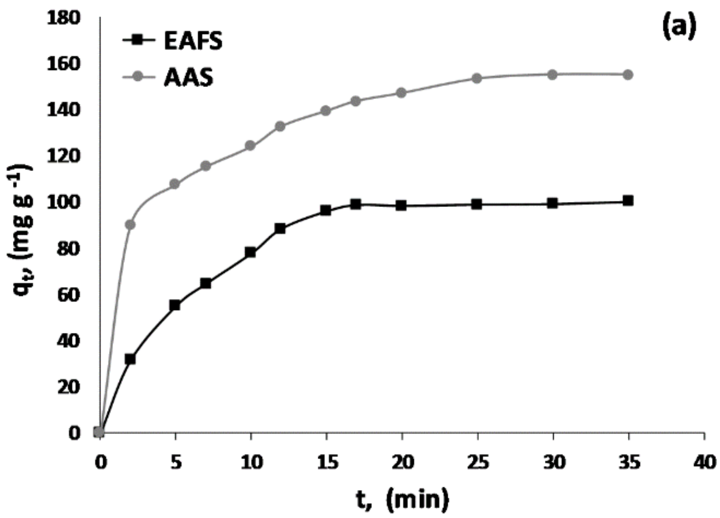
Pseudo first [13] and pseudo second [14] models were used to evaluate the adsorption kinetic (Eq. 2 and 3).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (2)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{3}$$

where k_1 (min^{-1}) is the rate constant of the pseudo first-order sorption, q_e is the amount of Cu^{2+} (mg g^{-1}) adsorbed on adsorbent at equilibrium and k_2 (g mg^{-1} min^{-1}) is the rate constant for pseudo second order model.

The results of kinetic investigations presented in the Table 1 and Figure 2b have shown that adsorption kinetic of Cu^{2+} ions by EAFS and AAS a better fit with the pseudo second-order model because the highest value of R^2 were obtained when this model was applied and the calculated values of q_e show a good agreement with the experimental values for q_e (Table 1). The results obtained indicate that adsorption of Cu^{2+} occur via chemisorption [15].



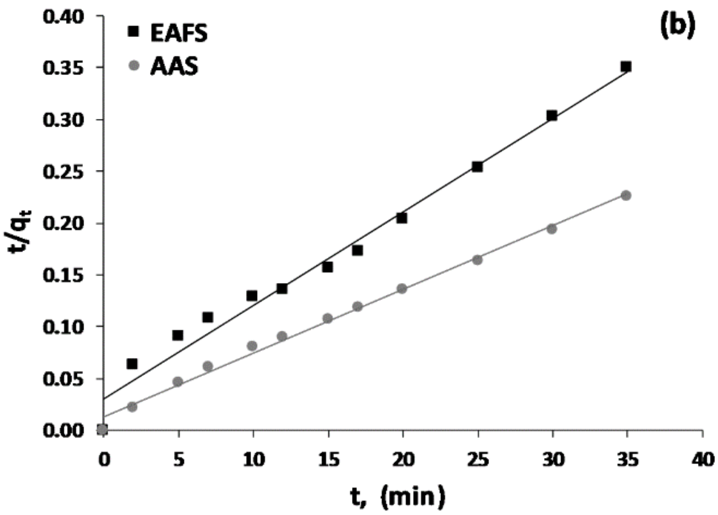


Figure 2 *Effect of contact time on the adsorption process (a) and second order plots (b)*

Table 1 *Kinetic parameters for the Cu^{2+} adsorption by EAFS and AAS*

Sorbent	Pseudo first order model				Pseudo second order model		
	$q_{e, exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	$k_2 \times 10^{-3}$ (g mg^{-1} min^{-1})	R^2
EAFS	98.44	112.12	0.18	0.972	101.11	2.71	0.982
AAS	153.05	130.92	0.20	0.943	161.29	3.13	0.994

CONCLUSION

This study demonstrated that the both adsorbents EAFS and AAS could be used as a new low-cost adsorbent for the removal of Cu^{2+} from wastewaters. The adsorption process is dependent on the pH of solution, initial Cu^{2+} concentration and contact time. Moreover, modification of EAFS by alkali activation improves the adsorption properties of EAFS.

The kinetic data showed that the pseudo-second-order kinetic model better fit with experimental results than pseudo-first-order kinetic model indicating that adsorption process onto both adsorbents is chemisorption in nature.

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MECHANICAL PROPERTIES OF A NEW INSULATION MATERIAL BASED ON *Miscanthus x Giganteus*

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Abstract

This paper deals with a brand new cost-effective, ecological and energy-efficient insulation material application based on Miscanthus x Giganteus with a reduced cement binder amount enriched with a smaller quantity of zeolite. In order to increase energy efficiency, the use of cement was minimized, as it is considered an extremely energy-inefficient material whose production requires large amounts of thermal energy, accompanied with high carbon dioxide emissions. As the physical-mechanical properties of thermal insulation are of crucial importance the paper deals with physical-mechanical properties of this material. The experimental part consisted of preparation of four mixtures with different component mass ratio, and determination of their physical-mechanical properties. The sample that showed the highest values of compressive and bending strength simultaneously was taken into thermal conductivity control tests. The thermal conductivity was measured by steady state conditions. The proposed composite material showed certain potential for practical and eco-friendly use.

Keywords: Energy efficiency, Insulation, *Miscanthus x Giganteus*

INTRODUCTION

The construction sector is one of the sectors with many problems in the field of environmental protection and sustainability, exploiting non-renewable resources, land use, energy consumption etc. [1]. It is one of the important segments of sustainable development and involves the use of eco-friendly and energy- and resource-saving construction materials.

This study deals with application of a brand new insulation material based on *Miscanthus x Giganteus* which is expected to be cost-effective and environment-friendly, as well as energy-efficient. In order to increase energy efficiency, the use of cement binder was minimized, since it is considered as an extremely energy-inefficient material consuming large amounts of heat for its production, with high carbon dioxide emissions [2]. Also, the use of this new material might significantly contribute to buildings energy efficiency, generally. For the purpose of this research, *Miscanthus x Giganteus* fibres were used instead of standard component materials. *Miscanthus x Giganteus*, also known as ”Elephant Grass“ or ”Chinese reed“, belongs to the family of grasses with many features of reed [3]. Originating from Asia, it was cultivated in Europe in the last century. During the vegetative season it can grow up to about 3 m in height and during this period the first yields are achieved, while for the complete establishment of plantations it takes up 3 to 6 years. After this period, a continuous rate of yield is achieved over a period up to 25 years without any demanding cultivation technologies during this period, making this plant extremely economical and easy to use [3]. Since manufacturing process is short, it has less carbon dioxide emissions, requiring lower energy consumption comparing to production of mineral wool or some synthetic organic (polymer) insulation materials [4]. Due to the morphological structure, a piece of stem provides a continuous process of micro-condensation and evaporation and has a certain level of self-thermoregulation, difficult to achieve with synthetic materials [5].

The standard thermal insulation materials have a thermal conductivity less than 0.06 W/(m·K) [6], such as already mentioned mineral and glass wool or expanded and extruded polystyrene [4]. The utilization capacity of *Miscanthus x Giganteus* products as insulating material could be expected, based on data of similar natural insulation such as hemp, wood or wood by-products, reed, straw, cotton, flax, etc. The insulation materials based on natural fibres have the thermal conductivity in the range of 0.038 – 0.090 W/(m·K) [4,7-9]. The investigation of insulation from the almost forgotten natural fibres have the great expansion due to its economical suitability and sustainability demands [4]. The new investigated material based on *Miscanthus x Giganteus* could be utilized as an insulation material or as a filler with satisfying thermal properties that might serve as cost-effective and environmental-friendly addition or replacement of conventional insulating materials, where it is possible.

MATERIALS AND METHODS

The new insulation materials based on *Miscanthus x Giganteus* were tested for physical, mechanical and trial thermal properties. The binder used for samples was a mixture of gypsum (3-5%), calcite (35-45%), slag (5-10%) and cement clinker (residue up to 100%). The prepared binder contained a reduced amount of cement clinker in relation to commonly used cement types. It has been enriched with a smaller quantity of synthetic zeolite. Zeolite shows good pozzolanic properties in alkaline medium, insulation properties (could be used in insulation coatings) and well absorbent performance [10]. It absorbs water and gasses, resulting in faster drying minimizing mold generation risk and release of unpleasant odours.

Although the thermal conductivity is the most important parameter of the insulating material, this study in the first place deals with physical and mechanical parameters which also have significant importance. The experimental part consisted of preparation of insulation material mixtures with different component mass ratio, determination of some physical parameters, mechanical properties investigations – compressive and bending (flexural) strength determination in the batch experiments and trial thermal conductivity tests.

Preparation of new mixtures for insulation material

The first experimental part was the preparation of four composite insulation material mixtures (marked I – IV) with the different component mass ratio, shown in Table 1. In order to prepare mixtures, *Miscanthus x Giganteus* chopped fibres, mineral binder, powdered zeolite and a sufficient quantity of water providing satisfactory workability, were used.

Table 1 *Mixture composition (mass ratio)*

Sample	$m_{Misc.}$ [g]	$m_{Bind.}$ [g]	$m_{Zeol.}$ [g]	$m_{Water.}$ [g]
I	300	420	180	360
II	400	420	180	360
III	300	480	120	360
IV	200	480	120	360

Miscanthus x Giganteus was previously air-dried for one month in the summer period, then fine-cut and shuffled. The chopped fibres were used with granulation of 300 mm with some possibly remaining pieces of long thinner fibres that could easily vertically pass through the sieve of this diameter. For the preparation of composites, the mentioned dry binder, powder zeolite and a sufficient quantity of water for incorporation into molds were used.

It is important to note that in the previous studies, *Miscanthus x Giganteus* proved to be resistant to the alkaline medium and the presence of silica. This information was important because the composite mixtures were prepared by mixing biomass and alkaline binder [11]. On the other hand, resistance to silicon dioxide is essential due to the subsequent usage and contact with standard construction materials such as, for example, mortar or concrete.

Determination of physical properties

The second part of the investigation was the determination of density, as the customary important physical characteristic. Low density means higher material' porosity and better insulation quality due to higher content of air which poorly conducts the heat [12].

It should be noted that there are other important physical parameters, such as absorption, water vapour diffusion resistance, thermal expansion coefficient, resistance to fire, chemical and biological stability, non-toxicity etc., which were not the part of this preliminary research.

The total (γ_u) and initial (after removing from the moulds) density (γ_0), as well as the density of the sample after drying during 90 days (γ_{90}) were defined according to equitation [13]:

$$\gamma_x = m_x / V_x \text{ [kg/m}^3\text{]} \quad (1)$$

where γ_x, m_x and V_x are corresponding density, sample mass and sample volume, respectively for each series sample.

Determination of mechanical properties

The third part of the experimental study was the investigation of mechanical properties by determination of compressive and bending strength in batch experiments. All mechanical tests were conducted in duplicate on 100 mm cubic samples, and in triplicate on prismatic samples (40x40x160 mm), shown in Figure 1. All results were presented as mean values.

Figure 1 *Samples for mechanical properties testing*

RESULTS AND DISCUSSION

Tables 2 and 3 show the mean values of density measured on cubic and prismatic samples.

Table 2 *Densities of cubic samples*

Sample	γ_u [kg/m^3]	γ_0 [kg/m^3]	γ_{90} [kg/m^3]
I	1205	1131	661
II	1298	1189	601
III	1223	1200	664
IV	1200	1135	619

Table 3 *Densities of prismatic samples*

Sample	γ_u [kg/m^3]	γ_0 [kg/m^3]	γ_{90} [kg/m^3]
I	1195	1086	715
II	1164	934	711
III	1211	1101	726
IV	1269	1285	851

Densities of all samples have higher values then mineral and glass wool or expanded and extruded polystyrene [12].

In addition to low density, it is important that the material has satisfactory mechanical properties.

The values of compressive strength of all samples were pretty different. For cubic samples, i.e. mixtures I and IV values were the highest (1.150 and 1.116 MPa, respectively). However, the values obtained on leftovers ("halves") of prismatic samples (remained after the bending test) only mixture IV showed satisfactory results (1.349 MPa). All results for compressive strength are shown in Figure 2a and b.

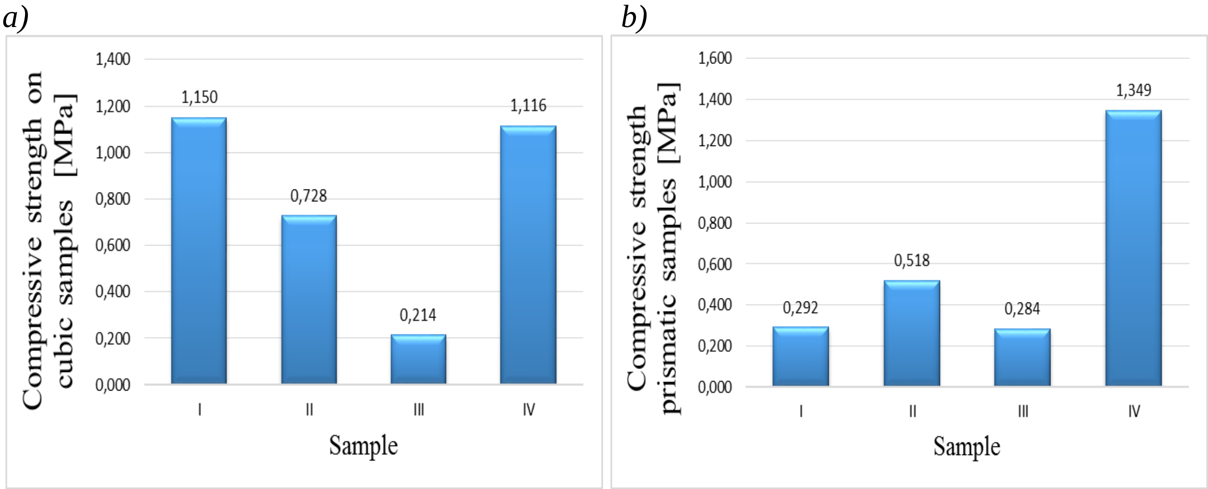

Figure 2 *Compressive strength [MPa]: a) on cubic samples; b) on halves from prismatic samples*

The similar trend was observed on prisms, priory subjected to bending test. Only mixture IV showed acceptable strength results with value of 0.631 MPa (Figure 3).

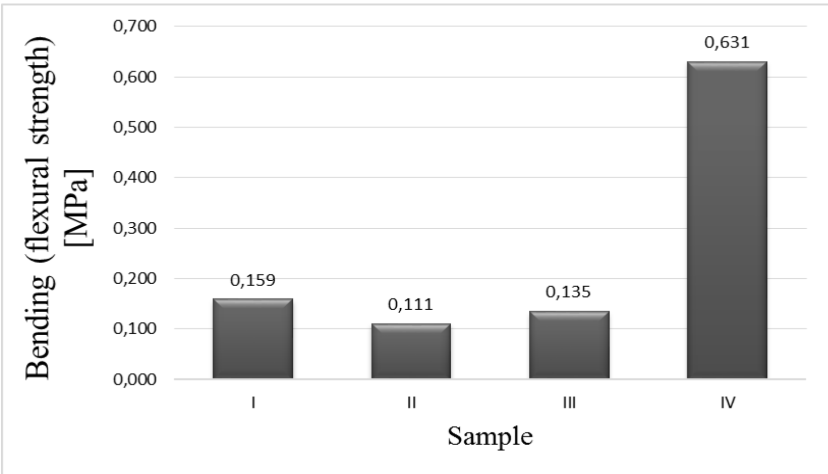

Figure 3 *Bending strength on prismatic samples [MPa]*

Since the mixture IV showed the highest values of compressive and bending strength simultaneously, only this mixture was taken into account for further thermal conductivity control tests. For thermal conductivity control tests, panel samples 500x500x70 mm were made (Figure 4). After drying up to a constant mass the selected panel had a thickness (width) of approximately 60 mm, and was tested.

Figure 4 *Sample for thermal conductivity determination*

The mean values of laboratory measured thermal conductivity for mixture IV panel, under the stationary thermal state conditions, were in the range 0.08 – 0.10 W/(m·K).

CONCLUSION

This research was conducted in order to prepare and investigate physical-mechanical properties of a brand new economical, ecological and energy-efficient insulation material. The four new mixtures based on *Miscanthus x Giganteus* fibres with a reduced cement binder amount and zeolite which shows good pozzolanic and absorbent properties, were prepared. In order to increase energy efficiency, the use of cement was minimized, since it is considered as an extremely energy-inefficient material, as well as high carbon dioxide emitter during its production. The utilization of this new material might significantly contribute to energy efficiency in construction sector.

The determination of densities has shown that all samples have higher values then mineral and glass wool or expanded and extruded polystyrene, i.e. smaller material' porosity.

The results of mechanical investigation on two cubic samples have shown good properties during determination of compressive strength, but only one mixture (mixture IV) has showed acceptable strength results for both strength tests (compressive and bending) with values 1.349 MPa and 0.631 MPa, respectively. Since only mixture IV showed the highest values of compressive and bending strength simultaneously, this mixture was taken into account for thermal conductivity control tests. The mean value of laboratory measured thermal conductivity was in the range 0.08 – 0.10 W/(m·K).

According to these results, examined composite material showed expected potential. It can be further enhanced with possible modification of its composition and preparation method in order to promote an additional reduction of its thermal conductivity.

ACKNOWLEDGEMENT

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ELECTRO-FLOCCULATION AS ONE OF THE ADVANCED METHODS IN WASTE WATER TREATMENTS

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Abstract

*This paper aims to provide some theoretical and practical knowledge of electro-flocculation as one of the advanced and more ecological clean method in treatment of waste waters. The application of iron and aluminum electrodes, with electrochemical reactions occurred on the anode surfaces, in electro-flocculation cell is shown. Construction of electro-flocculation reactors with electrodes arrangement for obtaining economical and most effective separation conditions are discussed. General conclusions from all our measurements is presented. Finally, the ecological benefit and limitation for application of electro-flocculation in industrial purposes are estimated***.**

Keywords: Waste water treatment, Electro-flocculation

INTRODUCTION

The surface water is the most used source in human life but it is very limited natural resource. Only about 0.3 % from total water on the planet belongs to the fresh surface water. With development of industry and human standard rapidly grows water pollution. Natural and waste water often contain dissolved and small solid particles that can be dispersed upon several forms. These forms depend on their size and could be: solution colloids and suspensions. The colloidal pollutants in waste waters contain: organic materials, metal oxides, insoluble toxic compounds, stable emulsions and biotic material including viruses, bacteria end algae [1]. Examples of colloidal systems include: milk (liquid fat droplets emulsified in water), paint (small pigment particles dispersed in a carrier fluid), aerosols (liquid droplets dispersed in air), and blood (the cells that flow through our veins are colloidal particles).

The removal of particles from a liquid is one of the basic types of separation in both drinking and waste water treatments. The particles are generally in the micron or sub-micron size range and are difficult to remove by sedimentation or filtration. It is necessary to increase the particle size by coagulation and flocculation. Coagulation is the process when colloidal particles and very fine solid suspensions begin to agglomerate. The second stage of the overall process of coagulation is flocculation and these two processes are closely connected. Flocculation is the process when coagulated particles conglomerate into larger aggregates (flocs) in two steps: transport and attachment, increasing significantly the weight, so they can be easily separated by conventional methods as: sedimentation, or flotation. The colloidal particles may be aggregated in microscopic particles by a coagulant and then these particles can be flocculated into a macroscopic floc. The flocs may then float to the top of the liquid, or settle by sedimentation to the bottom of the liquid (Figure 1). The rate of aggregation is determined by the rate at which inter particle collisions occur [2]. As the aggregates grow in size, hydrodynamic shearing forces can cause them to break up. These simultaneous processes lead to a steady state distribution of aggregate sizes. The aggregate structure will impact to the kinetics of the flocculation process. Flocculants are chemicals use to precipitate insoluble substances. The most used chemical compounds for flocculation are hydroxide and multivalent cations such as: hydrated aluminium, potassium sulphate, aluminium chloro-hydrate, calcium oxide, sodium aluminate, polymer salts etc.

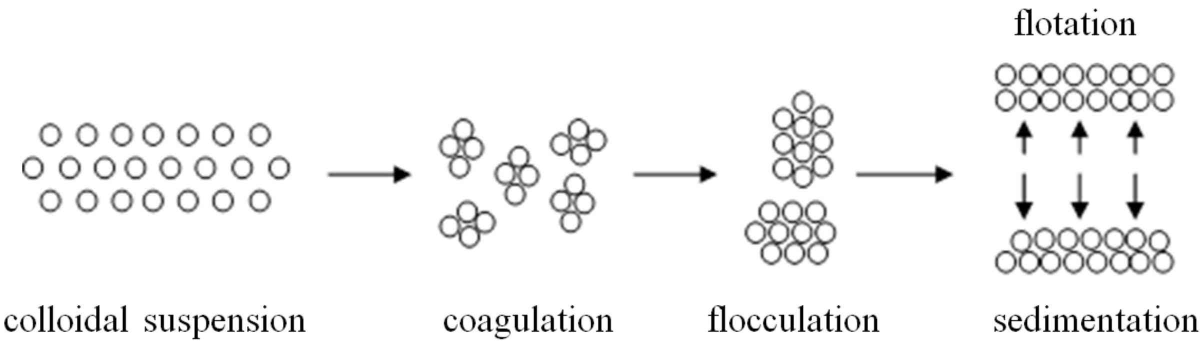

Figure 1 *Development the processes of coagulation, flocculation and sedimentation or flotation*

MATERIALS AND METHODS

Electro-flocculation

Electro-flocculation generally refers to the electrolytic addition of flocculating metal ions in the polluted water at the anode. For the process to occur, electrodes of the appropriate metal must be placed in water with an electric potential applied across the electrodes to cause an electric current to flow between them. The flocculating metal ions adhere to pollutants in the water, increasing their size as the stable flocs and then they can be easily removed.

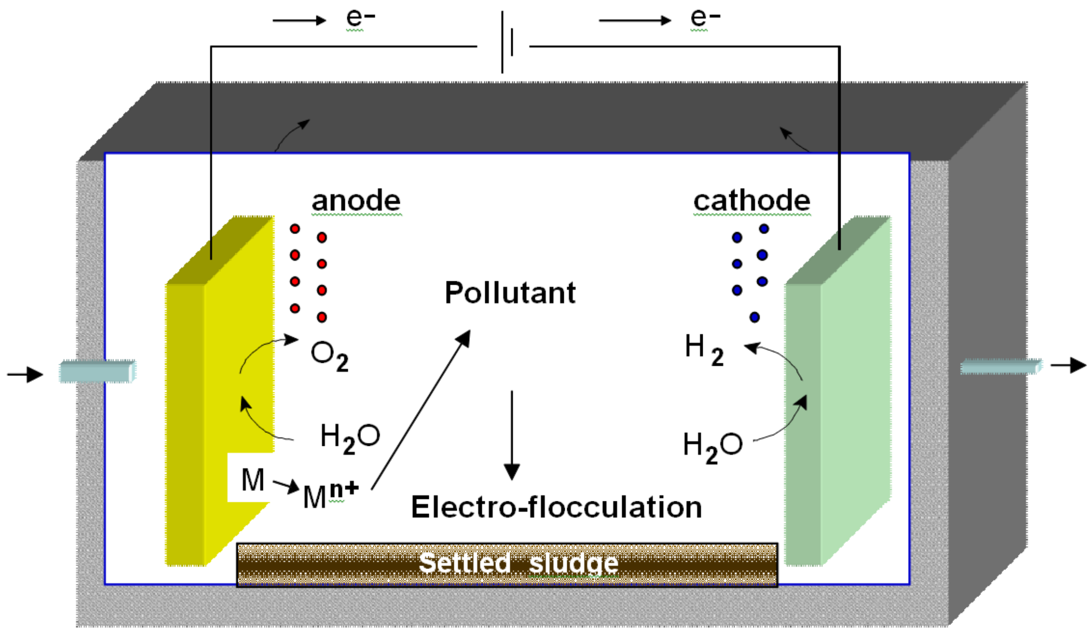

Figure 2 *Schematic presentation of experimental Set-Up for electro-flocculation process*

Our electro-flocculation unit consists of an electrolytic cell with an Al or Fe anode and stainless-steel cathode (Figure 2).

It should mention that we have also analysed many other electrodes like: steel, zinc, copper and different alloys but anodes from Fe and Al have shown the best properties. The electrochemical reactions occur instantly upon the passage of electrical current. Using the large surface area benefit the low voltages, typically between 2 and 4 volts, hence power consumption is also low. The electrode replacement is infrequent, several months to yearly intervals. The water's electrical conductivity has a major impact upon electrical power requirements and processing time. Lower conductivity required greater voltage or longer time needed for processing. In some types of waste water, if the conductivity is low, it is necessary to add some salts to increase the number of dissolved ions in the electrolyte. For this purpose we have used NaCl and $CaCl_2$. With reducing the distance between electrode will be also reduced the power consumption without changing the degree of separation. For a given pollutant type, the treatment is proportional to the amount of pollutant to be removed.

RESULTS AND DISCUSSION

Our measurements have confirmed that the most commonly used anode materials are iron and aluminium, because they produce trivalent ions. Other cheaper and more easily accessible metals produce bivalent ions. It should be pointed out that trivalent ions have a higher ability to be adsorbed onto particles in the water than bivalent ions, because they have a higher charge density. For iron anode, the destabilisation of colloidal particles could be performed with the assistance of the hydroxyl radicals which are generated during the ferrous-ion oxidation, according the reactions:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \tag{1}$$

$$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + HO_2^{\bullet} \tag{2}$$

$$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2 \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \tag{4}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^- \tag{5}$$

The oxidation of organic substrates by (Fe(II)) and hydrogen peroxide is called "Fenton reaction" [3].

For Al anode:

$$Al_{(s)} \rightarrow Al^{3+}_{aq} + 3e^- \tag{6}$$

In acidic electrolytes

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)} \tag{7}$$

In alkaline electrolytes

$$Al^{3+}_{(aq)} + 3(OH)^- \rightarrow Al(OH)_{3(s)} \tag{8}$$

Both Fe and Al trivalent ions form as proton donors $Fe(H_2O)_6^{3+}$ and $Al(H_2O)_6^{3+}$ which are only stable at low pH. At higher pH, they lose protons to form the monomers. Some of these

monomers are also unstable and try to form the OH bridged dimmer.

The settling velocity of multi fractal flocs formed in coagulation process has shown that a number of different mechanisms are involved in the formation of these flocs [3,4]. These mechanisms generally depend from the pH of the solution and potential applied during the electro-flocculation. For example two flocs with same size may have been formed by different mechanisms of aggregation and therefore have different arrangement of primary particles. Two flocs with the same size may have different masses or mass distribution and therefore, different settling velocity.

In practice the operation system for electro-flocculation consists of an: electrochemical reactor, electrodes, a power supply, pipes and pumps. It needs also to be automated with microprocessor control. This is required to make sure that changing conditions during the electro-flocculation do not prevent successful operation. It is necessary to adequately remove the pollutants that may settle to the bottom of the reactor. The design geometry of the reactor strongly influenced by the operational parameters including: effectiveness of the electro-flocculation, fluid flow regime, mixing and settling characteristics. The reactors typically have the cylindrical form and the quantity of inflow water must be balanced with the quantity of dissolved metal ions from anodes released in the reactor.

In practice two separate mechanisms for treating waste water by electro-flocculation: batch and continuous flow are used. Both systems involve a electro-flocculation reactor into which a set of electrodes (anodes and cathodes) are placed, (Figure 3).

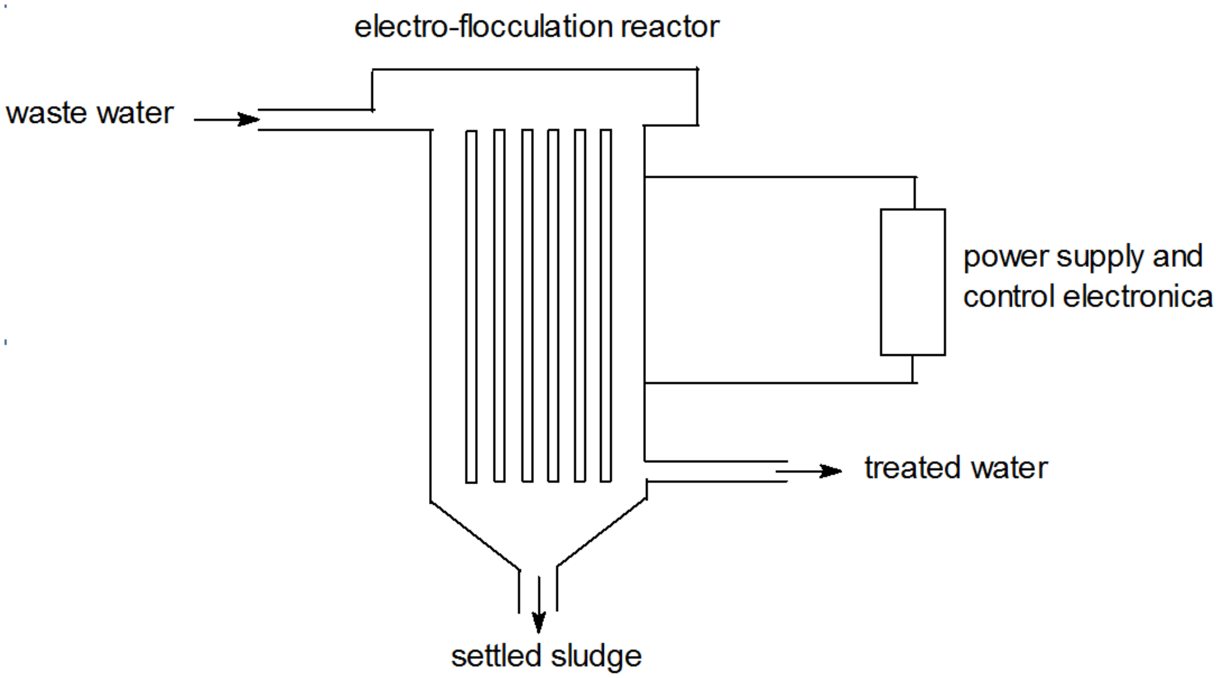

Figure 3 *Schematic presentation of electro-flocculation reactor*

In electro-flocculation reactors it is possible existing of two types of channel construction for water flow through the space between the electrodes: single or multiple channels, fig.4. The multiple channels are simpler to construct than a single, but the flow rate in each of the multiple channels is a smaller than in a single one. So far various authors proposed singles or multiples channels, depending of theirs experiments and type of electrode used. It should conclude that the type of channels depends also from specific characteristics of waste water and there is no unique recommendation.

Figure 4 *Mode of electrodes construction and water flow: (a) vertical single channel, (b) horizontal multiple channel*

In older reactors, the horizontal electrode design was use more frequently [5-8]. In now days the electrodes in the reactors are usually installed vertically. Anodes are placed at the bottom of the reactor, whereas the cathodes are fixed 10-50 mm above the anodes [9].

CONCLUSION

From our measurements that have been generally focused to the communal waste water the following conclusions can be drawn:

In many cases electro-flocculation has capability to overcome the disadvantage of the other treatment technologies. It is still an emerging technology which contains complex and multitude of mechanisms operating synergistically in combination with electrochemistry, polymer and surface chemistry, physicochemical properties of pollutants, effluents etc.

So far a lot of works have been consecrated to the electro-flocculation operating conditions. These conditions mostly depend on the chemical constituents and their concentrations, conductivity of wastewater, pH, particle size, type of used electrode, applied voltage, current density, retention time between electrode plates, plate spacing and number of electrodes.

The following contaminants can be removed by electro-flocculation: organic molecules with molecular weight greater then 300 g/mol, free and emulsified fats, oils, grasses and hydrocarbons, including benzene ring structures and many halogenated hydrocarbons, glues polymers and monomers, soap and detergents, as well as pathogens such as algae bacteria and viruses.

Many BOD and COD pollutants that consist of small organic molecules of molecular weight less than 150 are difficult to remove with electro-flocculation.

The most used electrodes are Fe and Al. It is still empirically optimized process. For each type of wastewater it is necessary firstly in laboratory conditions to optimize the working parameters. There is no yet generally the basic fundamental knowledge how to optimize the working parameters for each type of waste water.

There is no existing dominant reactor design. Materials for construction varied and adequate scale-up parameters have not been yet clearly defined.

There is no existing generic solution with passivation of electrodes. The formed passive films on electrode surfaces have semi-conducting properties and diminished the current efficiency.

Today electro-flocculation technique is widely used in treating industrial, rural, and communal waste water, but with variable success and certain limitation, especially in optimization and processes tuning. This technique is with higher efficacies in smaller cities where the installment of big equipment has not economical reason.

It should be pointed out that electro-flocculation is generally eco-friendly technology and has numerous advantages.

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SYNTHESIS AND APPLICATION OF THIOCARBAMATES OBTAINED BY OXIDATIVE TREATMENT OF WASTE XANTHATE

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Abstract

In this paper, the optimal treatment of industrial waste consisting from xanthate and oxidation product, i.e. diisobutyl and diethyl dixanthogenate, was developed for production of flotoreagents. Waste dixanthogenate was generated during production and storage of flotation agents, i.e. potassium isobutyl (KiBuX) and potassium ethyl xanthate (KEtX), respectively. The process of waste xanthate treatment is based on the reaction of the nucleophilic heterolysis of the persulfide bond in the diisobutyl dixanthogenates by alkylamines in presence of various oxidizing agents (sodium hypochlorite, hydrogen peroxide, potassium persulfate) to produce N-alkyl-, N,N-dialkyl- and N-cycloalkyl-O-isobutyl thiocarbamate selective flotoreagents. Also, analogous methodology was applied for synthesis of N-alkyl and N,N-dialkyl-O-ethyl thiocarbamate from KetX using sodium hypochlorite at laboratory and semi-industrial level. The developed method provides the corresponding alkyl thiocarbamates in a high yield and purity. The flotation efficiency was analysed using the obtained thiocarbamate on a real sample of minerals in laboratory and industrial conditions.

Keywords: Alkyl xanthate, Alkyl thiocarbamate, Dixanthogenates, Flotation

INTRODUCTION

Thiocarbamates are derivatives of thiocarbamic acid, *i.e.* salts and esters of thiocarbamic acids [1,2]. Structural characteristics, such as the direct bond between the thioacyl group and the nitrogen, contribute to their pronounced biological activity [3]. These compounds have a wide application thus they are produced at industrial level and used as fungicides [4-6], bactericides [5-7], herbicides [8,9], germicides [10], pesticides [11-13], and insecticides [14-16]. Also, alkyl thiocarbamates are used as polymerization accelerators and selective flotoreagents [17].

Besides the known procedures of thiocarbamates syntheses [18-22], many others were developed by reacting mono and dithiocarbonic acid-*O*,*S*-diesters with primary or secondary amine [23], alkaline xanthate, amine and oxidizer [24], thiol and isocyanate in the presence of a catalyst [25], sodium or potassium alkyl xanthates with aliphatic amines and sulfur [26], xanthates and amines in the presence of nickel(II) sulfate heptahydrate catalyst [27], oxidation of amine salts of xanthic acid with hydrogen peroxide or sodium hypochlorite [28], and oxidation of amine salts of dithiocarbamic acids with ammonium peroxodisulfate [29].

In this paper the optimal laboratory synthesis of *N*-alkyl-, *N,N*-dialkyl- and *N*-cycloalkyl-*O*-isobutyl thiocarbamate selective flotoreagents from industrial waste xanthate and the corresponding amines in the presence of various oxidizing agents: peroxide, sodium hypochlorite and potassium peroxodisulfate were presented. Waste xanthate from production of potassium isobutyl xanthate (KiBX) and potassium ethyl xanthate (KEtX) consists of starting xanthate and dixanthogenates [30]. Innovative procedure relate to optimal technological treatment which provided efficient conversion to thiocarbamate products. Second part of the work was related to synthesis of the *N*-alkyl and *N,N*-dialkyl-O-ethyl thiocarbamate from diethyl dixanthogenates in presence of sodium hypochlorite at laboratory and semi-industrial level. Moreover, the comparative study on flotation efficiency of the synthesized and commercial thiocarbamates for copper isolation from real mineral copper ore sample was performed.

MATERIALS AND METHODS

Synthesis of isobutyl thiocarbamate from KiBX and amines in the presence of potassium peroxodisulfate (Method 1)

Synthesis of isobutyl thiocarbamates was performed according to literature procedure [33]. The yield and purity of the products are determined by the GC method and are given in Table 1.

In a manner analogous to the procedure described above, the synthesis of thiocarbamate in the presence of hydrogen peroxide (Method 2) and sodium hypochlorite (Method 3) as an oxidizing agents was carried out [33], and the yields and purity of the products, determined by the GC method, are given in Table 1.

Synthesis of ethyl thiocarbamates from waste diethyl dixanthogenates

Synthesis of thiocarbamates from waste dixanthogenates, separated from waste xanthates, was carried out by reaction of the corresponding alkyl amines in the presence of sodium hypochlorite [34]. All other ethyl thiocarbamates are synthesized in an analogous manner to the procedure above, using the appropriate amines under reaction conditions presented in Table 2.

RESULTS AND DISCUSSION

Synthesized *N*-alkyl, *N,N*-dialkyl- and *N*-cycloalkyl-*O*-isobutyl thiocarbamate are characterized by FTIR, ^{1}H and ^{13}C NMR results, and obtained results are in accordance to literature data [30,33]. The purity is determined by the GC method and confirmed by elemental microanalysis. The yields and purity of the synthesized thiocarbamate, obtained by methods 1, 2 and 3, are shown in Table 1.

Based on the yields of the reactions products (Table 1), the most significant oxidation agent is potassium peroxodisulfate, and the yields are relatively similar and somewhat higher in oxidative processes than in those obtained by applying the conventional synthesis process of aminolysis of sodium isobutyl xanthogenacetate [30].

***Table 1** Yields and purity of synthesized isobutyl thiocarbamate*

Compound	**Yield** [%]			**GC purity** [%]		
	H_2O_2	NaOCl	$K_2S_2O_8$	H_2O_2	NaOCl	$K_2S_2O_8$
iBuOC(S)NHEt	87.2	85.1	90.3	98.5	98.3	98.6
iBuOC(S)NHPr	88.6	86.5	91.7	97.3	97.5	97.2
iBuOC(S)NHnBu	89.5	86.8	92.6	99.0	99.1	99.2
iBuOC(S)NHsBu	89.3	87.2	92.4	99.4	99.3	99.1
iBuOC(S)NHiPr	87.1	85.0	90.2	99.2	99.0	99.2
iBuOC(S)NHiBu	93.6	92.5	96.7	97.0	97.2	97.8
iBuOC(S)NHiPent	94.1	92.0	97.3	97.5	97.7	97.9
iBuOC(S)NHcPr	77.4	75.6	80.2	97.8	98.0	98.6
iBuOC(S)NHcPent	83.6	82.4	86.7	98.0	98.1	98.5
iBuOC(S)NHcHeks	87.7	85.6	90.8	97.0	97.2	97.9
iBuOC(S)N(Et)$_2$	93.8	91.7	96.5	97.4	97.6	97.5
iBuOC(S)N(Pr)$_2$	95.2	94.0	98.0	98.0	98.1	98.8
iBuOC(S)N(Bu)$_2$	95.9	95.1	98.2	97.0	97.2	97.9

Waste diethyl dixanthogenates treated with various alkylamines in the presence of sodium hypochlorite oxidant gave ethyl thiocarbamate product (Table 2).

***Table 2** Yields and purity of N-alkyl and N,N-dialkyl-O-ethyl thiocarbamate*

Compound	**Reaction time** [h]	**Temperature** [^oC]	**Yield** [%]	**GC purity** [%]
EtOC(S)NHMe	2.0	30 - 45	89.2	97.9
EtOC(S)NMe$_2$	2.0	30 - 45	90.0	97.8
EtOC(S)NHEt	2.0	30 - 45	88.0	97.0
EtOC(S)NEt$_2$	2.0	30 - 45	88.8	97.6
EtOC(S)NHPr	2.0	30 - 45	88.2	98.0
EtOC(S)NPr$_2$	3.0	40 - 50	84.5	98.4
EtOC(S)NHi-Pr	3.5	40 -55	82.1	99.6
EtOC(S)Ni-Pr$_2$	4.5	40 - 55	75.0	98.9

Based on the results presented in Table 2 high yields and purity of *N*-alkyl and *N*, *N*-dialkyl-*O*-ethyl thiocarbamate were obtained, and depends on the structure of the amines used. Voluminosity of di-*n*-propyl, isopropyl, and di-isopropyl group contributes significantly to steric repulsion which prevents amines to performe an effective nucleophilic heterolysis of S-S bonds in the first step of the reaction. Amine structure has essential impact on the nucleophilicity of amines [31]. Lower yields were obtained for *N*,*N*-di-propyl-*O*-ethyl thiocarbamate (84.5%), *N*-isopropyl-*O*-ethyl thiocarbamate (82.1%), while lowest for *N*-diisopropyl-*O*-ethyl thiocarbamates (75.0%). MS, FTIR, ^{1}H and ^{13}C NMR data are in accordance with literature [31]. The amount of sulfur produced after the filtration of the reaction mixture corresponds to the theoretical stoichiometric value in relation to the starting quantities of the reactants.

In accordance to optimal laboratory synthesis semi-industrial production was carried out at H. I. Župa Kruševac plant. It was found that the reaction products are not present in waste water, while the concentration of dixanthogenates is below the maximum contamination limit, Table 4 [32]. Necessary wastewater treatment is also very simple. An innovative method could be widely used for the synthesis of thiocarbamate starting from various raw materials: ammonium salts and alkaline salts of *O*-alkyl xanthic acid [33], as well as waste or commercial diethyl dixanthogenate [34]. The results of the implementation of the defined method at the semi-industrial level are shown in Table 3.

***Table 3** Results of semi-industrial synthesis of N-ethyl-, N-propyl and N,N-dipropyl-O-ethyl thiocarbamate*

Thiocarbamates	Reactants								Reaction conditions		By-product	Product		
	Amine		H_2SO_4		Sodium ethyl xanthate		NaOCl		t	T	Sulfur	Yield		GC
	kg	kmol	kg	kmol	kg	kmol	m^3	kmol	h	°C	kg	kg	%	%
EtOC(S)NHEt	35.4	0.55	28.1	0.28	144	1.0	0.66	1.5	2.5	30.0	25.0	126.5	95.0	99.0
EtOC(S)NH(nPr)	33.2	0.55	28.1	0.28	144	1.0	0.66	1.5	2.8	30.0	24.0	135.2	92.0	98.6
EtOC(S)N(nPr)$_2$	54.4	0.55	28.1	0.28	144	1.0	0.66	1.5	4.0	30.0	20.0	161.0	85.2	98.1

The technological scheme of the semi-industrial process for the synthesis of thiocarbamate is presented in Figure 1. Results of determination of isobutyl dixanthogenate in wastewater in the process of semi-industrial production are presented in Table 4.

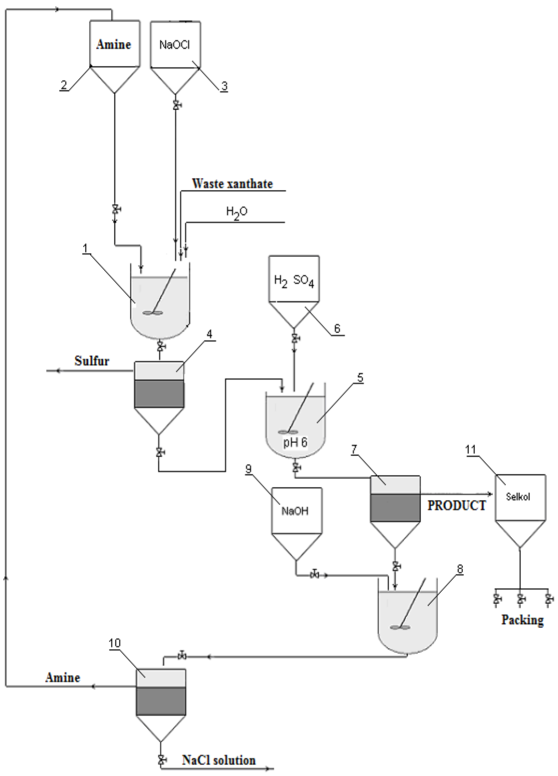

***Figure 1** Technological scheme of the semi-industrial synthesis of ethyl thiocarbamate*

***Table 4** Concentrations of ethyl dixanthogenate in waste water*

Compound	Sample amount [cm^3]	Concentration of ethyl dixanthogenate	
		c ·10^3 [mmol dm^{-3}]	**c ·10^2** [mg dm^{-3}]
EtOC(S)NHEt	70.00	21.36	58.00
EtOC(S)NHnPr	85.00	20.09	53.80
EtOC(S)NHiPr	85.00	19.98	54.31
EtOC(S)NHBu	80.00	18.45	50.29

The product obtained by the defined procedure was examined in the flotation process on a real mineral sample. The results of comparative studies on flotation efficiency, synthesized versus commercial, of copper ore sample from the Elacite-Bulgaria are presented in Tables 5 and 6.

Table 5 *Flotation results obtained using commercial N-ethyl O-isobutyl thiocarbamate*

	W, [g]	**w,** [%]	**Cu,** [%]	**Cu,** [g]	**ICu,** [%]
Entrance	996.9	100	0.454	4.5284	100
BCCu	36.9	3.70147	11.350	4.1881	92.4845
KKCu	14.5	1.4545	1.030	0.1493	3.2980
UKCu	51.4	5.1560	8.438	4.3375	**95.7820**
Tailings	945.5	94.8440	0.020	0.1909	**4.2175**

****W*** *- weight of ore sample,* ***w*** *- mass % of ore sample,* ***ICu*** *-copper content* ***BCCu*** *-basic concentrate,* ***KKCu*** *- prolonged flotation,* ***UKCu*** *-total flotated copper,* ***Tailings*** *– copper content in tailings.*

Table 6 *Flotation results obtained using synthesized N-ethyl O-isobutyl thiocarbamate*

	W, [g]	**w,** [%]	**Cu,** [%]	**Cu,** [g]	**ICu,** [%]
Entrance	1000.6	100	0.460	4.6088	100
BCCu	40.5	4.0475	10.820	4.3821	95.0794
KKCu	12.2	1.2192	0.810	0.0988	2.1441
UKCu	52.7	5.2668	8.502	4.4809	**97.2230**
Tailings	947.9	94.7332	0.013	0.1279	**2.7765**

Based on the results shown in Tables 5 and 6, it can be seen that synthesized flotoreagents are more efficient flotation reagent. Analogous comparative study was carried out with real copper ore sample from JAMA - Bor mine, and obtained results are given in Tables 7 and 8.

Table 7 *Flotation results obtained by using commercial N-ethyl O-ethyl thiocarbamate*

	T, [g]	**t,** [%]	**Cu,** [%]	**Cu,** [g]	**ICu,** [%]
Entrance	990	100	0.657	6.5072	100
UKCu	195	19.6969	3.123	6.0906	**93.5981**
Tailings	795	80.3030	0.052	0.4165	**6.4018**

****Kcu*** *– flotated copper by basic flotation,* ***Tailings*** *– copper content in tailings.*

Table 8 *Flotation results obtained using synthesized N-ethyl O-ethyl thiocarbamate*

	T, [g]	**t,** [%]	**Cu,** [%]	**Cu,** [g]	**ICu,** [%]
Entrance	995	100	0.696	6.9346	00
UKCu	210	21.1001	3.1385	6.5908	**95.0418**
Tailings	785	78.8912	0.044	0.3438	**4.9581**

The obtained results on the flotation efficiency related to the real copper ore sample from JAMA-Bor mine, Tables 7 and 8, showed higher flotation efficiency of synthesized thiocarbamate comparing to commercial one.

CONCLUSION

Synthesis of *N*-alkyl-, *N*,*N*-dialkyl- and *N*-cycloalkyl-*O*-isobutyl thiocarbamate from amine salts of xanthic acid obtained from KiBX separated by waste xanthate treatment with potassium peroxodisulfate, hydrogen peroxide and sodium hypochlorite. Highest yields in presence of $K_2S_2O_8$ (80.2-98.2%), lower in the presence of H_2O_2 (77.4-95.9%), and the lowest in the presence of NaOCl (75.6-95.1%). The process for the synthesis of *N*-alkyl and *N,N*-dialkyl-*O*-ethyl thiocarbamate from waste diethyl dixanthogenates and amines in the presence of sodium hypochlorite was developed at the laboratory level and applied at the semi-industrial level. The structures of all synthesized thiocarbamates were confirmed by FTIR, ^{1}H and ^{13}C NMR spectroscopy, as well as MS spectrometry. The purity was determined using GC chromatography and elemental analysis. This new environmentally acceptable process represents a favorable possibility for existing methods, and offere a significant contribution to environmental protection. The results of comparative studies related to flotation efficiency from copper ore samples showed higher percentage of flotated copper using synthesized thiocarbamates in comparison to commercial one.

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CHARACTERISTICS OF FLY ASHES, THEIR POTENTIAL USES AND DAMAGED CONDITIONS OF LANDFILL DEPOSITS

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Abstract

Diverse industries produce fly ashes as thermal power plants, waste incinerators, and some recycling processes. Though some of these products can be raw materials for diverse applications, their composition can be hazardous due to their content in heavy metals. In addition, mixing fly ashes with the products of neutralization of fumes complicates the products. Then many fly ashes are landfilled in a Portland-cement matrix. However, most of the actual knowledge about their ageing derives from models the validity of which has been established only on the short term, using small sized proofs, at room conditions while matter transfers and reactions are strongly affected by temperatures reaching 80 °C for many years. Ageing leads to a mobility of chlorides, sulphates and lead, alteration of textural properties with formation of microcracks, formation of neo-formed minerals as silicate-hydrates (katoite and hibschite, CSH), carbonates, tobermorite, hydrogarnets zeolites,…) that can contribute to bear Pb, Zn, Cr, Cu, in addition to inherited phases (metallic alloys, spinels, glasses, refractory oxides, titanates, phosphates,…). The alkaline hydrolysis of aluminium in saline media decreases the pH and promotes the precipitation of lead species trapped in a hydrocalumite or ettringite matrix.

Keywords: Fly ashes, Cement based matrix, Long-term evolution

INTRODUCTION

Municipal waste treatment, thermal power plants and some elimination-beneficiation devices devoted to decayed composite materials produce fly ashes. The incineration of municipal waste is currently used to reduce volume, recover energy, reuse materials and control residues. The so-called Municipal Solid Waste Incinerator (MSWI) fly ashes also contain added materials as neutralizing products of fumes, and then high content of inorganic mobile components as chlorides, sulphates and heavy metals. Due to their fineness and their high inorganic pollutants potential, the MSWI are hazardous materials that cannot be valorized nor recycled, in Western Europe, their production reaches about 1.2 10^6 tons/year, what generates environment problems; solidification/stabilization (S/S) industrial methods have been developed to solve them. The S/S process based on hydraulic binders is often used to stabilize MSWI fly ashes [1]. In this procedure, the solids are usually mixed with cement and water or with bitumen, with or without other additives (lime, pozzolanic reagents…) and, finally, mainly disposed in landfills, producing huge monoliths also called monofills [2].

Three classes of such landfills exist, the class 1 is devoted to hazardous materials. The question of potential utilizations of MSWI fly ashes (fillers in concretes [3], material for ceramics…) is also explored and need to know their long-term behavior.

MSWI fly ashes S/S involving hydraulic binders has been used for years, however, its long-term durability remains an open question. Most of the knowledge about the element mobility depends on models the validity of which has been established on the short term, using small sized proofs, at room conditions [4,5]. A difficulty remains to build mobility models for monofills submitted to weathering, since the porosity and the nature of phases evolve over time. This study aims at clarifying the mineralogical status of several heavy metals, mainly Pb, Zn and Cr, and anions, as SO_4^{2-} and Cl^-, to predict their long-term behavior. Others elements as Cd, As and Hg, also impact the environment, they volatilize during combustion, condense on the finest particles and occur at low local concentrations [6], approaching their speciation needs a high-resolution determination that will not be considered here.

Two disposal sites were considered. One, with MSWI fly ashes stabilized with Portland cement without any previous treatment was ten years old (site A); the other, with MSWI fly ashes stabilized with cement after a partial leaching and precipitation of soluble heavy metals using Na_2S, was five years old (site B). In both monofills, the S/S MSWI fly ashes have not been covered so that they have been submitted to atmospheric weathering. Aged samples were also compared with fresh materials and small test-bars.

MATERIALS AND METHODS

Raw residues were collected from the filters and gas scrubbers of the two incineration plants. For the residues corresponding to the site A, the filter fly ashes and the gas scrubber salts were collected separately, while the sample of the site B is a mixture of fly ashes and salts. Sampling of the site B was performed using a hammer-drill, since core-drilling was impossible, due to the poor cohesion of the materials. The monoliths were sampled from top to bottom. Small test-bars (A) realized by mixing the raw MSWI residues with Portland cement and water were also analyzed.

The quantities of samples taken from site B with the drilling-machine were not sufficient, because of drilling problems. Thus, the monolith was trenched, and the trench sampled. During excavating, an important release of water vapor was noticed, which indicates a high temperature inside the monolith. Furthermore fresh blocs of solidified/stabilized MSWI fly ashes obtained in the plant B have also been analyzed.

Characterization analyses are detailed in Antenucci *et al*., [7] and summarized in *Yvon et al*., [8], they concern chemical bulk analyses, compliance tests, permeability, mineralogy, petrographic analysis and micro-analysis by SEM or TEM.

RESULTS AND DISCUSSION

According to chemical analysis and compliance leaching tests, the bulk concentrations of Pb and Zn are rather high, high leached amounts of Pb and Zn are measured from the raw materials. For the solidified materials, the highest leached amount is displayed by Pb, whereas Zn is systematically leached below the European regulation limit. In some cases, leached amounts of Cr exceed the accepted limit. The SO_4^{2-} leached quantities are often above the European limit whereas the Cl^- leached concentrations are systematically higher.

Compared with classical concretes, the solidified MSWI fly ashes show a high permeability. The water drain-off through test-bars ranges between 4000 and 6500 cm^3 instead of 11 cm^3 in case of a convenient concrete. Such elevated values result of the low cohesion of the material. Despite the lake of porosity measurement, this high permeability depicts a risk of mobilization of toxic elements by weathering.

The petrographic analysis exhibits common texture and composition of the samples. Networks of micro-cracks, related to hydration-dehydration cycles and/or to shrinkage, and reactions with dissolution at very high pH and/or replacement by portlandite, sulphates, titanates or hydrocalumite are observed. No carbonation discrepancy was observed between the various aged samples at the scale of polarizing microscope.

Based on XRD the materials A and B, contain the same mineral phases. The salts A are mainly enriched in $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$, portlandite and calcite, while the fly ashes contain calcite, halite, sylvite, fluorite, anhydrite, quartz, hematite, magnetite and pyrite. Portlandite, calcite, $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$, sylvite and halite are present in the A samples. Only calcite remains as a major mineral in B, but in the fresh S/S MSWI B, portlandite and calcite are the main inherited phases. Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) and hydrocalumite ($Ca_2Al(OH)_6(Cl,OH) \cdot 3H_2O$) are formed by weathering in all the S/S MSWI, and katoite ($Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$), gonnardite, ($Na_2CaAl_4Si_6O_{20} \cdot 7H_2O$) and tobermorite ($Ca_5Si_6(O,OH)_{18} \cdot 5H_2O$) in B. No mineralogical discrepancy has been observed between cored and trenched samples. Both the test-bars and fresh samples are free of katoite, gonnardite and tobermorite. Since the mineralogical analysis does not reveal any vertical gradient concerning calcite, the carbonation has minor effects.

Neither the raw MSWI residues, nor the S/S MSWI fly ashes contain any pollutant bearing minerals, indicating that those phases are either absent, amorphous or under the detection limits. Thus TEM and SEM were involved to complete the XRD characterization. The back-scattered electron imaging shows that generally these particles are finer than 10 µm, SEM-EDS and TEM-EDS analyses indicate the presence of metals in different inherited or neo-formed minerals. The pollutant bearing minerals in the two sites are rather analogues, except sulphides that are more present in B due to the sulphidation pre-treatment.

Among the inherited phases: the stable phases are glasses containing zinc, lead and chromium, metallic alloys, spinels, oxides, hydroxides, phosphates containing lead and zinc, mainly those of the apatite group, zinc titanium oxides and zinc silicates. The inherited unstable phases are amphoteric metals, calcium chromates, hydroxy-chlorides and chlorides more abundant in the A samples.

Except for hydrogarnets, katoite or hibschite, that contains some Zn, the other major neo-formed phases, hydrocalumite and ettringite are free of transitional cations. Considering the minor neo-formed phases, actually ordered silicates hydrates (afwillite) and hydrotalcite group minerals, only the later contains some Zn. The limited cationic substitution observed in these minerals is in contrast with the data reported in the literature [9-13].

Some minor neoformed phases are stable as diverse Ca/Zn titanates, zinc phosphate (hopeite), Zn and Cr in barium sulphate (hachemite), mixed Pb/Cu/Hg sulphides, and mixed Pb/Cu hydroxysulphates. Some others are unstable as lead chlorides and hydroxychlorides, lead hydroxide, resulting from the hydrolysis of aluminium followed by the precipitation of aluminium hydroxide, hydrocalumite, and hydrocerusite.

The incorporation of Pb and Zn in the CSH compounds corroborates the data reported in the literature [13]. However, samples B show that Pb occurs mainly as PbS that precipitates during the pre-treatment.

The petrographic approach reveals a network of connected micro-cracks that explains the high permeability of solidified materials, promote fluids circulation, facilitating the leaching and the chemical reactions, then the removal of pollutants.

The presence of hydrocalumite and ettringite in the solidified samples explains the behavior of Cl^- and SO_4^{2-} under leaching. Hydrocalumite is a soluble mineral at any pH, the Cl^- leached amounts are not drastically lowered by the S/S process and, then, the solidified MSWI fly ashes behaves as hazardous material with regard to Cl^-. The ettringite solubility decreases when pH increases [14], the SO_4^{2-} leached amounts are significantly reduced compared to the starting raw material, but are often above the accepted European limit. Thus, ettringite cannot ensure an ideal immobilization of SO_4^{2-}.

The temperature measured *in situ* when sampling the site B was close to 70°C. In monofills, the temperature probably reaches 100°C, what generates a convection of fluids. This phenomenon can arise from slow or differed exothermic reactions without fast evacuation of energy. The temperature and the circulation of fluids promote the crystallization of ordered silicate-hydrates, namely zeolites, hydrogarnets and tobermorite. Natural Si-rich hydrothermal solutions are known to promote the crystallization of silicate-hydrates in fractures and cavities where katoite, ettringite, tobermorite, afwillite, chabazite, etc., crystallize [15].

Temperature indications are also supported by data available in the literature. Gonnardite, is synthesized between 100 and 120°C from coal fly ashes [16], and tobermorite can be stable between 80 and 140°C [17]. Usually the hydration of concrete minerals generates disordered hydrates, named CSH, that trap one significant part of soluble zinc and lead, and bring a low permeability to the whole in such a way that soluble lead and zinc salts can crystallize in vacuoles [18]. In the present cases, the ordered hydrates are almost free of metallic pollutants, lead is concentrated in leachable phases and micro-cracks increase the permeability.

Despite the fact that no *in situ* temperatures have been measured for the site A, the presence of hydrocalumite, as a major phase, as well as hydrotalcite and Zn-hydrogarnet, as minor phase, suggest temperatures close to those indicated for the site B. Several layered double hydroxides (LDHs), [12-19], have been synthesized in hydrothermal conditions between 65 and 110°C [20,21]. The test-bars reveal drastically less heavy metal-bearing mineral species. By analogy with the above considerations on silicate-hydrates major phases, such a result shows that the differentiation of minor species also requires a prolonged exposure to high temperature. This information is particularly indicative of the limit of reliability of models established at laboratory scale, from which the long-term behavior of solidified/stabilized MSWI fly ashes in cement matrix are deduced.

Pb, Zn and Cr are distributed between different phases: inherited stable phases (metallic alloys, spinels, glasses, refractory oxides, titanates, phosphates…), inherited or neo-formed unstable phases (amphoteric metals, hydroxides, carbonates, chlorides, chromates…). The neo-formed Pb-chloride and oxy-chlorides identified in solidified/stabilized materials are linked to the hydrolysis of aluminium, which leads to the following systematic sequence: aluminium (core zone)/aluminium hydroxide (intermediate zone)/hydrocalumite (external zone). Pb-minerals, smaller than 1 µm, crystallize inside the hydrocalumite zone [7,8].

No cationic substitution occurs in ordered silicate-hydrates compounds, except for katoite where some Zn^{2+} substitutes for Ca^{2+}. In addition, the heavy metals-bearing minor minerals display cationic substitutions involving Zn and/or Cr, but do not show substitutions involving Pb. The fact that ordered silicate-hydrates are essentially free of Zn and Cr ions indicates that a significant part of these cations are fixed irreversibly in the starting materials, through the formation of spinels, glasses, refractory oxides, etc., at high temperature, their high stability explains the low leached amounts of Zn and Cr. The fact that some samples display Cr leached concentrations higher than the European acceptable limit is due to the soluble chromate minerals. The question of Pb needs a more extended discussion. It is well known that Pb^{2+} often substitutes for Ca^{2+}, as in phosphates of the apatite group [22,23] or arsenates, such as tsumcorite, (Ca, Pb)(Zn, Fe^{2+}, Cu^{2+}, Mn^{3+}, $Co)_2$ $(AsO_4)_2$•(H_2O, $OH)_2$ [24]. To explain the unexpected observed results, the electronic configuration of Pb must be considered [25]. The one-sided arrangement of bonds to anions is typical of the stereochemically active $6s^2$ lone-pair behavior for Pb^{2+}, which leads to quite irregular Pb polyhedra. In particular, this situation can be observed in various Pb-oxy-chlorides, for instance those displaying the common thorikosite-type structure, $Pb_3SbO_3(OH)Cl_2$, which includes, among others, symesite, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$ [25], pinalite, $Pb_3(WO_5)Cl_2$, and blixite [26], where the active $6s^2$ lone-pair effects manifests by drastically decreasing the average Pb-O bond length and increasing the average Pb-Cl bond length in the Pb-sites [25]. Available crystallographic data for katoite [27], ettringite [28] and hydrocalumite [29] indicate regular Ca-sites, suggesting an incompatibility with the geometry required by the electronic configuration of Pb^{2+}. Thus, the crystallochemistry constrains combined with the high activity of Cl^- and the basic pH in the cement-based solidification/stabilization, promotes the crystallization of Pb-species, favouring the precipitation of unstable Pb-minerals. This situation is responsible for the high level of leached Pb in A samples. In the samples B, given the pretreatment of raw materials the activities of Cl^- and S^{2-} are reduced and Pb can be partially incorporated in more stable sulphide minerals such as PbS. Furthermore, the Pb-hydroxides, Pb-chlorides and oxy-chlorides, the most abundant Pb-bearing phases, are trapped inside hydrocalumite zones that are more micro-cracked in A than in B samples [7]. As a consequence, in the B S/S MSWI fly ashes, the unstable Pb-minerals are temporary screened by the hydrocalumite zones: a situation that promotes a time-lag Pb leaching off.

CONCLUSION

The compliance leaching tests cannot predict, alone, the long-term evolution of pollutants in MSWI fly ashes solidified/stabilized in cement matrix. Monofills of solidified/stabilized MSWI fly ashes using hydraulic binders are affected by a prolonged exposure to temperature close to 100°C that governs the evolution of major mineral phases and the differentiation of metal bearing minor ones. Disordered hydrates form at low temperature, they trap one part of heavy metals and generate a low permeability barrier. At high temperature hydrates are ordered, do not accept heavy metals in their lattice and generate a highly porous barrier. The zinc and in part chromium bearing phases are stable, whereas mineral species containing lead, Cl^- and SO_4^{2-} are unstable, despite the maturation. Finally, the solidification/stabilization of MSWI fly ashes through hydraulic binders is rather not the right solution with regard to SO_4^{2-}, Cl^- and Pb. At present time, given their hazardous character due to the instability of lead and anions-bearing phases, the S/S MSWI fly ashes must be managed in landfills devoted to hazardous wastes.

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SORPTION OF COPPER BY FLY ASH

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Abstract

This study is occupied by using fly ash for copper removal from the acid mine wastewater and synthetic solution of the similar composition. Chemical analysis of mine wastewater proved that the values of Cu, Zn, Fe, and Mn exceed the maximum accepted concentration in a large extent. Serbian fly ash from "Nikola Tesla" power plant was used as a low cost sorbent for removal of copper ions (Cu^{2+}) from aqueous solutions. Fly ash was subjected to the elementary and XRD analysis. As a method, batch sorption procedure was applied. Sorption efficiency was studied as a function of the contact time, and amount of the sorbent. Equilibrium was determined after 90 min for all investigated sorbent dosages.

Keywords: Copper, Sorption, Fly ash

INTRODUCTION

Heavy metals are released into the environment finding the way to get into the water-streams and thus make an environmental contamination that presents threat to humans, animals, and plants. This can cause serious diseases and complex disorders [1].

Acid mine waste water (drainage) is significant environmental problem since it contains high concentration of toxic and heavy metals such as copper, nickel, cadmium, lead, iron, manganese, and zinc. Amount of these metals exceed maximum acceptable concentration (MAC). Today, heavy metals are most serious pollutants, becoming a severe public health problem. During the mining process of copper exploitation, large amount of waste water is generated. The chemical composition of these waste streams is very complicated and depends on the chemical composition of the ore that leaches during the exploitation. At the Cerovo and Krivelj deposits, RBB-RTB Bor, one of the biggest problems presents the generated lake at the open pit. At this moment, the estimated amount of the "Cerovo lake" is 600.000.000 dm^3 (and it grows every day) of this water with the average content of 200 mg Cu^{2+}/dm^3. The mathematical calculation leads us to the fact that only in this lake 120 tonnes of copper is trapped [1,2].

Concentrations of heavy metals in the wastewater and water-streams have to be reduced in order to satisfy rigid legislative standards. They can be removed by various technologies, most often expensive or inefficient and technically complicated especially because of limited maximum accepted concentrations required by the EPA (Environmental Protection Agency) [1-3]. The conventional techniques for heavy metals removing from aqueous solutions include oxidation, reduction, chemical precipitation, filtration, ion exchange, adsorption, membrane techniques, electrolytic or liquid extraction, reverse osmosis, biological process [3,4].

Each of these methods is used only in special cases since it has some limitations in practice [4,5]. Namely, the major disadvantages of almost mentioned methods are production of new hazardous waste, mostly solid, at the end of the treatment as well as high cost of sorbent and applied technique [1]. Among these processes, the adsorption is a simple and effective technique for the removal of heavy metals form wastewater. Nowadays, many researchers are occupied by development of new low cost materials and methods for the treatment of wastewater containing heavy metals, for example natural adsorbents such are zeolites, wood, lignite, metal oxides, fly ash, coal, and waste biomass [1,4,5]. In general, sorbent can be characterized as a low cost if it requires little processing, is abundant in nature or is a by-product of industrial activities. Hence, industrial by-products are almost zero-cost materials and at the same time their utilization could contribute to the solution of their management problem improving the material efficiency within the several industrial activities. Predominant mechanism in this process is ion exchange, but also there is surface adsorption, chemisorption, complexation and adsorption-complexation [1-5].

Fly ash has potential application in wastewater treatment because of its major chemical components (alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon), and its physical properties such as porosity, particle size distribution and surface area. Besides, the alkaline nature of fly ash makes it a good neutralizing agent [1,2]. Namely, fly ash as a potential hazardous solid waste produced like a by-product in power plants worldwide in million tonnes has attracted researches interest for years.

The objective of this study is possibility of using domestic fly ash on ability for removing the heavy metals from synthetic aqueous solution and acid waste drainage water. Batch sorption experiments were conducted to characterize and model the sorption equilibrium.

Since the copper industry is one of the biggest in the field of the heavy metals and, at the same, there is a big copper producing facility RTB Bor in Serbia, the main accent in this paper, was put specifically on the removal of this metal.

MATERIALS AND METHODS

Sample characterization

The fly ash used in the experiments was collected in power plant Nikola Tesla, Obrenovac, without any pre-treatment. It remains as a residue from lignite combustion recovered from cyclones and electrostatic filters of the power plant.

Chemical and XRD analysis of the fly ash were done and shown in this paper. The XRD method was used to determine the phase composition. The XRD patterns were obtained on a Philips PW 1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 4 to 65^o, counting for 0.5 s (qualitative identification) at every 0.02^o step. The divergence and receiving slits were fixed 1 and 0.1, respectively. All the XRD measurements were performed at room temperature in a stationary sample holder.

Mining wastewater originated from the generated lake at the open pit Cerovo deposit, RBB-RTB Bor. Synthetic aqueous solution was prepared too by dissolving the appropriate amount of $CuSO_4$ in deionized water.

Sorption experiments

The kinetic experiments were performed at room temperature using the batch technique under the continuous stirring conditions. The procedure was as follows: weighted amount of sorbent was placed into a glass vessel with cover. Prepared synthetic or "real" solution was added. Volume of the solutions was constant (100 dm^3), as well as the stirring conditions. The effectiveness of different amounts of sorbent was observed during the experiment (2, 6, and 10 g of fly ash). Experiments were monitored periodically up to 120 min. In order to quantify sorption efficiency, suspension was filtered and residual copper concentration in the filtrate was determined by Perkin Elmer Atomic Adsorption Spectroscopy, type "PinAAcle 900T (Perkin Elmer)" instrument.

RESULTS AND DISCUSSION

Characterization of wastewater

Almost all previous researches were occupied with the sorption of heavy metals realized by usage of synthetic solutions. However, the real problem arises in case when the heavy metals should be removed from the real system of mining wastewater.

Chemical analysis of acid mine wastewater located at "Cerovo Lake" is shown in Table 1.

Table 1 *Chemical analysis of acid mine waste water*

Content (mg/dm^3)												
Fe	Mn	Zn	Cu	Pb	Ni	Cd	Cr	Cl^-	SO_4^{2-}	SiO_2	CaO	MgO
70.5	30.0	50.0	168.0	0.8	0.5	0.36	0.01	0.018	3.69	87.76	601.66	543.0

Analyzed wastewater is acid aqueous solution with pH of 3.15.

Chemical analysis of synthetic aqueous solution that imitated the real wastewater is given in Table 2. pH of the synthetic aqueous solution was 2.87.

Table 2 *Chemical composition of synthetic aqueous solution*

Content (mg/dm^3)			
Fe	Mn	Zn	Cu
70.6	34	49.5	171

Characterization of sorbent

Chemical composition of fly ash is shown in Table 3. The results of chemical analysis showed that the main and most important components of the fly ash are silica, alumina, as well as calcium and iron oxides with smaller amounts of magnesium, alkalies, and traces of many other elements.

***Table 3** Chemical composition of fly ash*

Content (%)							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2
47.8	30.53	5.47	8.69	2.29	1.49	0.25	1.02
Cd	Pb	Zn	Cu	Cr	Ni	Mn	LOI
0.005	0.04	0.021	0.005	0.022	0.03	0.045	1.45

XRD analysis of fly ash was done and results showed presence of quartz, mullite, and plagioclase, Figure 1.

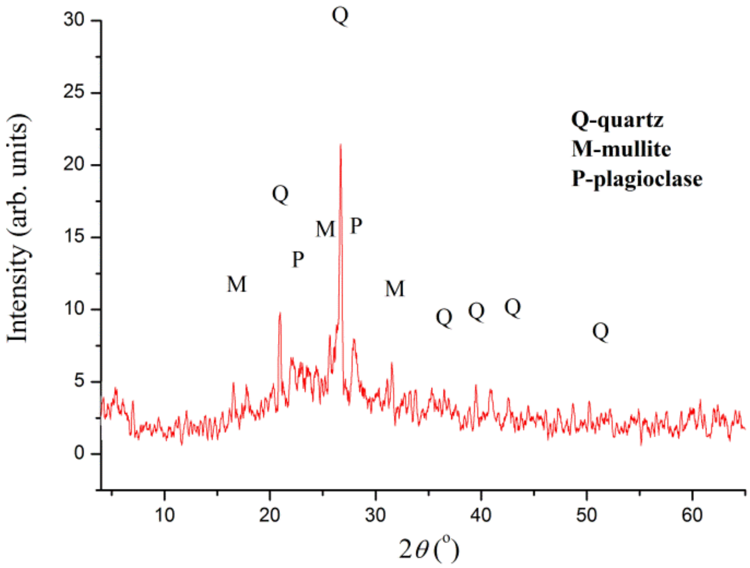

***Figure 1** XRD pattern of fly ash*

The major mineral phase is quartz, while the mullite and plagioclase are present as an accessory minerals and their effect on physicochemical behavior of the minerals are limited. The presence of magnetic phase was detected in analyzed sample, but there was no one reflection to match this phase. Since the level of crystallinity is very small, portion of amorphous phase is significant.

Kinetics experiments

The effects of sorbent dosage and contact time on sorption process at 20 ± 2°C were studied. Initial batch studies conducted to assess the time taken for the equilibrium to be attained. The solution-sorbent mixtures were shaken and at the end of predetermined time intervals (5, 30, 60, 90, and 120 minutes) their content was filtered and the filtrates were analyzed for the content of Cu. The influence of the other present metals will be investigated and analysed in some further papers.

As it presented, the sorption of Cu onto fly ash showed typical two phases kinetics with rapid sorption period during the first 5 minutes followed by a slower one. During the initial stage of sorption, a large number of surface free sites are available for sorption whereas, with gradual occupancy of these sites during the sorption process, it becomes difficult to be attracted to the sorbent due to repulsive forces between the sorbate molecules on solid surface and in the liquid solution. Besides, a driving force of mass transfer between the liquid phase and the solid phase of fly ash decreases with the time, which also results in the slowing down of the sorption during the later phase of sorption. The chemical constituents of fly ash affect its sorptive properties towards metal cation. Therefore, an attempt was made to establish a relationship between the sorption capacity of the fly ash and its major chemical constituents, such as mineral oxides (calcium, aluminium, and silica oxides) and carbon. As assumed herein, the fly ash is a dual sorbent that means it sorbs by both mineral and carbon. Copper removal by fly ash was achieved through the competitive sorption between carbon and mineral [3].

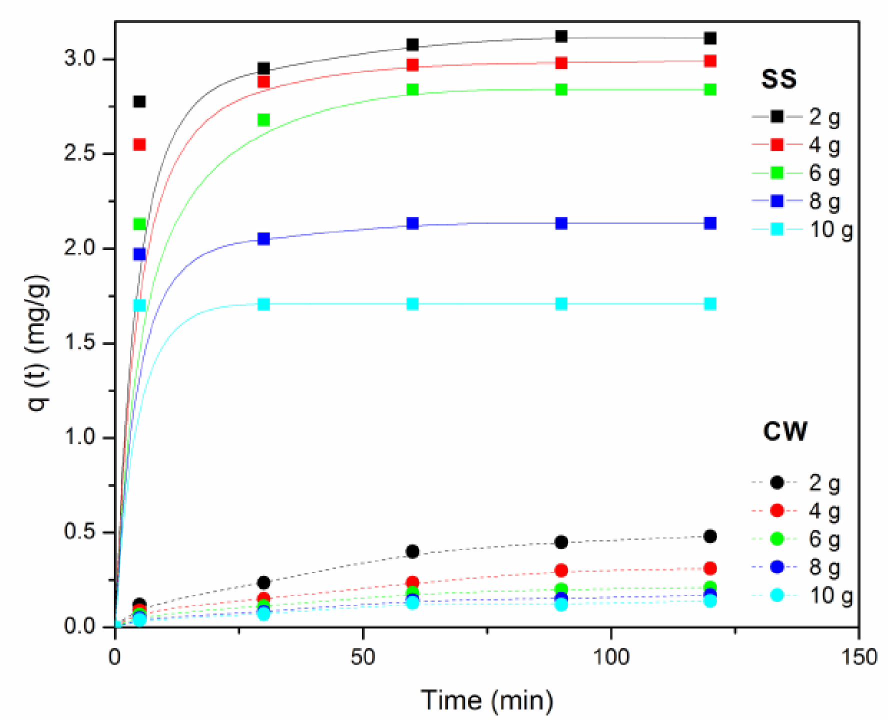

Figure 2 *Sorption of Cu on fly ash from complex aqueous solutions (SS-synthetic solution and CW-Cerovo Wastewater) depending on time*

The effect of sorbent dose on the removal of heavy metals shown in Figure 2 displays that sorption capacity, as expected, decreases with sorbent dosage. The higher amount of the sorbent results in a better Cu removal. However, due to the higher competitiveness of the active centers for the sorption, the sorption capacity decrease.

The sorption of copper from the synthetic solution was significantly higher compared with the sorption from the real wastewater. This is mainly due to the presence of many other ions that are presented in a real wastewater, unlike the synthetic solution. In order to increase the effectiveness of the removal from the real wastewater, certain pretreatment should be considered in a future.

CONCLUSION

This work concerns the removal of Cu^{2+} ions from the multi-complex solutions by fly ash. The influence of two parameters (fly ash dosage and contact time) on the removal of heavy metal ions commonly encountered in mining wastewater was reported. It was found that copper was sorbed onto the fly ash very rapidly (within the first 30 min), while the equilibrium was reached in 90 minutes. Higher dosage of the sorbent leads to higher effectiveness and the lower sorption capacity.

Sorption efficiency of all tested metals dosages was considerably higher in a synthetic solution compared to the real system.

ACKNOWLEDGEMENT

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THE SURFACE MODIFICATION OF ALUMINA PARTICLES FOR ITS APPLICATION IN UNSATURATED POLYESTER RESINS

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Abstract

Alumina particles, received as a fine nano-scaled powder, were modified by chemical treatment in order to improve the efficacy of reinforcing application. The modification procedure is performed in two consecutive steps: i) with 3-(aminopropyl)trimethoxysilane (APTMS) and ii) with methyl ester of linseed oil - BD. Further on, pristine and modified materials were used as a filler/reinforcement in unsaturated polyester resin (UPR) matrix, which was synthesized from poly(ethylene terephthalate) (PET) waste. The effect of incorporation of pristine/modified alumina particles was investigated varying the amount of alumina particles in the range of 0.1-2.0 wt%, as well as mechanical properties of pure UPR and composites with corresponding fillers. The best enhancement of tensile strength was achieved with filler amount up to 1.0 wt%, while micro Vickers hardness was significantly improved for each alumina loading. In this study, the obtaining of a new/eco/multi functional materials for potential application in industry, mining and construction is examined.

Keywords: Alumina, Modification, Reinforcement, Unsaturated polyester resin, Mechanical properties

INTRODUCTION

A different types of reinforcements can be used in thermosetting matrices, where great efforts for designing a suitable composite formulations result in obtaining of materials with unique properties [1,2]. Nano-sized alumina powders, with excellent structural, optical and electrical characteristics are adequate candidates for the preparing of polymer nanocomposites [3]. The hydrophilic nature of alumina nanoparticles leads to high moisture absorption, formation of agglomerates and incompatibility with hydrophobic segments of polymeric matrices [4]. These disadvantages were most frequently overcome by surface modification of alumina nanoparticles, using silane coupling agents [5,6]. The obtained structures enable the establishment of a great linkage with polymeric matrices, especially with those which contain double bond segments, such as unsaturated polyester resins (UPR).

UPRs are the most frequently used thermosetting matrices for the obtaining of high performance composite materials. The UPR production can be performed by re-use of the waste poly(ethylene terephthalate) (PET) in respecting the circular economy, green production and sustainable development concept [7,8]. However, UPRs have some deficiencies such as high brittleness, which can be overcome by incorporation of the functionalized reinforcements into the polymer matrix. Functional groups attached at the filler surface participate in cross-linking reactions during curing of thermosetting resins resulting in obtaining the improved mechanical properties of corresponding composites [9,10]. The influence of modification type/amount of alumina particles on mechanical properties of UPR based composites is investigated in presented study.

EXPERIMENTAL PART

Materials

The pristine nano alumina, 1,2-propylene glicol (PG), tetrabutyltitanate (TBT) styrene, toluene, pyridine, methyl ethyl ketone peroxide (MEKP), cobalt octoate, maleic anhydride (MA) and solvents, toluene and tetrahydrofuran (THF), were received from Sigma Aldrich. The 3-(aminopropyl)trimethoxysilane (APTMS) was purchased from Dynasylane, Evonik Industries. All chemicals were used as received without further purification.

Synthesis of UPR

UPR was synthesized from waste poly(ethylene terephthalate) (PET) by glycolysis with PG and afterwards polycondensation between obtained polyol and maleic anhydride. The thoroughly described procedure for UPR synthesis from waste PET can be find elsewhere [1,11].

Surface functionalization of alumina particles

Alumina particles were modified with APTMS (first step) and biodiesel - BD, prepared according to previously published method (second step) [2]:

- *First step - modification with APTMS*: Alumina particles (1.0 g) were placed in reactor and dispersed in toluene for 5 min. Afterwards, 4.0 g of APTMS was added reaction was carried-out in the next 48 h at 25 ºC under nitrogen atmosphere. Modified alumina was separated from solvent by vacuum filtration, washed with toluene and dried.
- *Second step - modification with methyl ester of linseed oil - BD*: The modified alumina from the first step was dispersed in THF. Further on, 1.6 g of BD was charged into reactor and reaction was continued for the next 12 h at 25 ºC. Afterwards, the reaction mixture was heated up to 60 ºC and maintained for 2 h. The final product was filtered under the vacuum, washed with THF and absolute ethanol and dried at 40 ºC for 12 h.

Preparation of composites based on UPR and alumina particles

Composites, UPR/Al_2O_3(n), were prepared by mixing the determined amount of UPR resin and alumina particles. Index n designates the amount of added filler into UPR matrix: (a) 0.1, (b) 0.25, (c) 0.5, (d) 1.0 and (e) 2.0 wt%. The procedure for compounding the polymer matrix and reinforcements is thoroughly described in the previously published studies [1,2].

Experimental techniques

The structural analysis of pristine/modified alumina particles was 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}. 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. The hardness of the composites was characterized using micro Vickers hardness (HV) tester Leitz, Kleinharteprufer Durimeti with a load of 4.9 N.

RESULTS AND DISCUSSION

FTIR

The FTIR spectra of pristine/modified alumina particles are shown in Figure 1, where the influence of modification process on tailoring the filler surface is investigated.

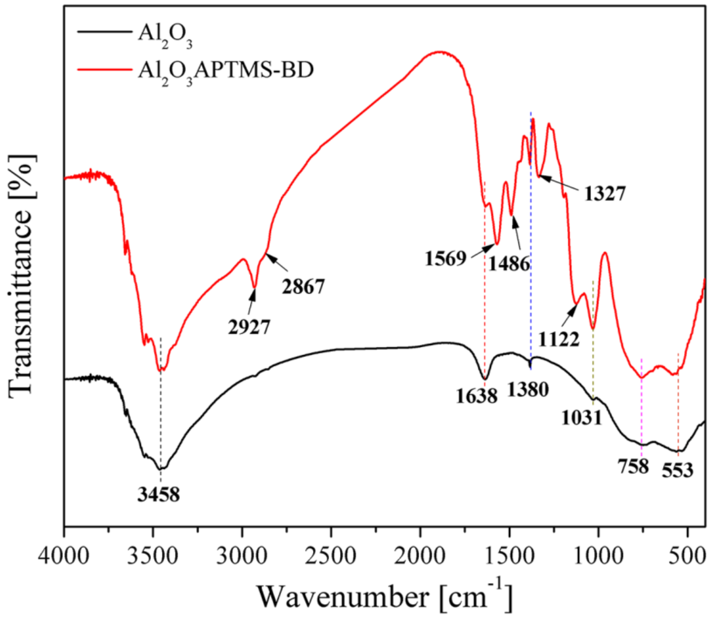

Figure 1 *FTIR spectra of pristine and modified alumina particles*

The characteristic peak at about 3450 cm^{-1} and 1638 cm^{-1}, remarked for both pristine and modified alumina particles, is attributed to stretching vibrations of hydroxyl groups [12]. The specific broad bands in the range of 550 - 750 cm^{-1} is related to Al-O-Al and Al-O vibrations [13].

In the FTIR spectra of modified alumina particles, the remarked peaks around 2927 and 2867 cm^{-1} originate from CH_3 and CH_2 stretching vibrations, respectively. The stretching ν(N-H) vibrations, overlapped with Al-O-Al and OH tapes, are observed at about 800 and 3450 cm^{-1}, while bending N-H vibrations are detected at 1569 cm^{-1}. Symmetrical C-H deformation vibrations of CH_3 are remarked at 1486 cm^{-1}. Peak, shown at 1380 cm^{-1}, originates from bending vibrations of CH_2 groups. Stretching vibrations of C-O from ester groups which originate from BD are observed at 1122 cm^{-1}. FTIR analysis confirms successfulness of alumina modification using APTMS/BD.

Mechanical properties of composites based on UPR and alumina particles

Mechanical testings are performed in order to determine the influence of addition the pristine/modified alumina particles on tensile strength and micro Vickers hardness of UPR based 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 tabulated in Table 1. All obtained results are discussed in respect to mechanical properties related to pure UPR.

Table 1 *Tensile stress at break (σ_t), elongation at break (ε_t), tensile modulus (E_t) and micro Vickers hardness of UPR and corresponding 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/Al_2O_3(a)	31.14±1.34	3.80±0.14	0.84±0.07	37.21±0.63
UPR/Al_2O_3(b)	35.09±1.48	4.31±0.15	0.82±0.08	39.16±2.32
UPR/Al_2O_3(c)	36.59±1.64	3.55±0.14	1.06±0.12	41.60±1.04
UPR/Al_2O_3(d)	41.65±1.13	4.81±0.13	0.96±0.05	49.63±3.63
UPR/Al_2O_3(e)	30.54±1.55	3.04±0.13	0.96±0.11	38.38±2.45
UPR/Al_2O_3APTMS-BD(a)	30.78±1.34	3.40±0.14	1.01±0.08	58.78±2.20
UPR/Al_2O_3APTMS-BD(b)	32.25±1.52	3.64±0.13	0.98±0.09	71.94±1.29
UPR/Al_2O_3APTMS-BD(c)	38.44±1.73	4.13±0.16	1.02±0.10	86.56±10.86
UPR/Al_2O_3APTMS-BD(d)	40.79±1.66	4.37±0.19	1.06±0.11	107.07±0.94
UPR/Al_2O_3APTMS-BD(e)	25.80±1.27	2.43±0.12	1.08±0.11	60.65±1.39

Table 1 shows that incorporation of pristine and modified alumina particles significantly improves the tensile strength of UPR based composites. The improvement is manifested in the similar fashion regardless to the type of alumina particles; gradually increases up to 1 wt% of added reinforcement afterwards the significant decrease is remarked. The achieved enhancement of σ_t is in range 12.3 - 33.4% and 3.3 - 30.6% for incorporation of Al_2O_3 and Al_2O_3APTMS-BD compared to pure UPR resin, respectively. According to data for ε_t, more flexible materials are obtained by incorporation of both types of alumina particles (pristine and modified), which is reflected in decreasing of tensile modulus, E_t. These results reflect the contribution of chemical interactions established between functionalities of fillers and UPR resin. Pristine alumina nano-particles are effectively distributed in UPR matrix which enables obtaining the materials with uniform composition, without physical weak spots. Besides, surface OH groups establish hydrogen bridges with oxygen from carbonyl groups in UPR resin which additionally improves the interfacial alumina/polymer matrix interactions. Modification of alumina particles with system APTMS/BD introduces the unsaturation spots and some amount of free amino functionalities. Unsaturated/double bonds from modified alumina participate in establishing the covalent linkage with double bonds in UPR resin which originate from maleic anhydride and styrenic segments. Contrary to this, the geometry of modified alumina particles, which are substantially larger than pristine, leads to steric hindrance and thus the weakening of interfacial interactions. That is the main reason for achievement the somewhat lower tensile strength improvement by incorporation of modified alumina particles into UPR matrix.

Contrary to this, the improvement of HV is significantly higher for addition of modified filler into UPR resin. The enhancement of HV is in range 47.6 - 96.9% and 133.2 - 324.7% for the incorporation of Al_2O_3 and Al_2O_3APTMS-BD alumina compared to pure UPR resin, respectively. The remarkable improvement achieved by addition of pristine/modified alumina particles is contribution of covalent/hydrogen bonds interactions between fillers and polymer matrix. Such outstanding HV results obtained by Al_2O_3APTMS-BD incorporation is probably the consequence of entanglements formed from BD segments which thickening the material and thus increasing the resistance to intender penetration.

CONCLUSION

The main purpose of this work is to investigate reinforcing effect of pristine/modified alumina particles when they are incorporated in UPR matrix synthesized from waste PET. According to obtained results, significant improvement of tensile strength and micro Vickers hardness of corresponding composites are achieved, compared to pure UPR resin. Moreover, the synergy of two different materials (PET and alumina) is accomplished which justifies the usage of alumina reinforcement in this kind of application.

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CHARACTERIZATION OF CARBONACEOUS MATERIAL FUNCTIONALIZED WITH SILVER OBTAINED BY HYDROTHERMAL CARBONIZATION

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Abstract

Carbonaceous materials functionalized with silver were obtained in one –step process by hydrothermal carbonization of plane tree seeds. The plane tree seed ball comprises a dense spherical cluster of achene with a tuft of many thin stiff bristle fibres attached to the base of each achene. This material is proven to be a very promising raw material for carbon materials that serve as catalyst support as well as adsorbent for harmful substances. The aim of this study is to examine which part of this seed ball contributes the most to the desired properties. Achene and bristles separated and mixed as well as only the bristle fibers were examined. The silver nitrate has been used as a source for silver. The obtained carbonaceous materials functionalized with silver were characterized as follows. The presence of silver was confirmed by X-ray diffraction. The textures of these materials before and after carbonization were examined with scanning electron microscopy. The antimicrobial activity of these materials was also examined. All the samples showed the satisfactory antimicrobial activity.

Keywords: Plane tree seed, Silver, Hydrothermal carbonization, Antimicrobial effect

INTRODUCTION

Carbon materials can be made from any organic compound or material. Also they could be obtained by various production techniques such as: pyrolysis under an inert atmosphere, chemical vapor deposition, chemical vapor impregnation, isostatic pressing, arc discharge, hydrothermal process etc. [1-6]. Due to the huge number of different raw materials and various synthetic methods, a wide range of carbon materials could be obtained. In the last decade an old and almost forgotten technique became very popular, because it contributes to the preservation of the environment in several ways. First of all, it enables the production of carbon material at much lower temperatures than with the application of the pyrolysis process, and more importantly, the synthesis is done in a closed system, thus preventing the emission of gases into the environment. It is hydrothermal technique or hydrothermal carbonization process (HTCP) which is actually a green technology.

HTCP was created by Bergius in 1913 as a mimic of the natural coalification process, but with a drastic duration reduction which could take hours and days. However, nowadays the focus of HTCP is shifted to the production of nanostructured and functional carbonaceous materials. This process allows the possibility of using cheap, readily available and even renewable precursors such as saccharides or biomass [7-14].

Carbonaceous material especially activated carbonaceous material have a wide range of applications. Activated carbon is widely used in environmental protection for adsorption of pollutants from gaseous and liquid streams, for recovery of solvents, in catalysis as a catalyst support, in electrochemistry, medicine, etc. [1-6].

Activated carbons and silver have been used in medicine used for centuries in the treatment of burns, wounds and skin infections. Medical applications of activated carbons are based on their powerful adsorption capacity. They are used to remove harmful toxins from the human body. Due to the bactericidal and bacteriostatic activity of silver ion, it is commonly usually used as an antimicrobial agent in the form of nitrate, acetate or organic compound silver-sulfadiazine [15,16].

Generally, a great challenge in the field of material production is to produce material from cheap and readily available and renewable raw material by low cost process. That could be easily realized in activated carbon material production [17].

The Plane tree bristly seed, besides low cost, are renewable raw material with the unique fibrous structure. So, it is a promising raw material for the preparation of activated carbon material. The fruit matures in about 6 months, to 2–3 cm diameter balls. After being pollinated, the female flowers become an achene (small dry indehiscent (remaining closed at maturity) one-seeded fruit), which united with the others on the flower-head to form the spherical fruit. Fruit balls hang in clusters of two to six and comprise a dense spherical cluster of achene with numerous stiff hairs which aid wind dispersal. The cluster breaks up slowly over the winter to release the numerous 2–3 mm seeds. Achene is about 1 cm long and 1 mm thick [14,18,19].

In this study the plane tree seed were used as cheap and suitable raw material together with silver nitrate. Seeds have been used for preparation of activated carbonaceous materials functionalized with silver. The HTCP process was used to get a desired material in a one-step process. The antimicrobial potency of obtained materials was examined. The aim was to examine which part of the plane tree seed contributes the most to the desired properties.

MATERIALS AND METHODS

Materials

The plane tree seed were collected from *Platanus orientalis* growing in Belgrade (Serbia) parks. Collected plane tree fruits were cut open to take the inside achene (Figure 1a) and separate the bristles from achene. Bristles and achene could be better seen in Figure 1b.

a)

b)

***Figure 1** Plane tree fruit: a) cut open with many achene inside; b) bristles attached to the base of each achene [19]*

The silver nitrate has been used as a source for silver. Silver Nitrate [$AgNO_3$] in a crystal form and nitric acid were purchased from Centrohem, Stara Pazova, Serbia.

Methods

Sample preparation

Plane tree seed balls were cut open and washed with distilled water to remove dust and dirty. After that the samples were dried in dry oven. The bristles were separated from achene and prepared three types of samples: whole seed denote as PTS, only achene (PTA) and only bristles (PTB). The samples were ground in a coffee mill for easier handling during the experiment. Each of these samples (5 g) was put into the 40 ml of the 7.38 mM $AgNO_3$ solution of 0.1M solution of HNO_3. The mixture was than stirred on magnetic stirrer for 60 min and after that the mixture was put in a stainless steel autoclave which was then placed in a dryer oven. After hydrothermal carbonization at a temperature t = 260 °C and maintained for 65 h, the precipitate was collected by filtration and then washed repeatedly with distilled water and ethanol. Finally, the resulting product was dried in a dryer oven. Carbonized samples were denoted by adding C before previous notifications and become CPTS, CPTA and CPTB.

Sample characterization

The presence of silver was examined by X-ray diffraction-XRD. The textures of these materials were examined with scanning electron microscopy (SEM). The antimicrobial activity of these materials was also examined. All the samples were tested for removing pathogenic bacteria from the brook. Samples of water were collected during the winter season and plated LB-agar Petri dishes (50µL of water on 8cm Petri dish) in triplicate. The incubation at 37°C in microbiological incubator last for 36h. The number of colony forming units (CFUs) was determined simply by counting from the photographs before and after samples adding. Plates are photographed after 48 hrs, for better visualization. Number of CFU represents the number of viable microorganisms (without identification) in the initial volume of water sample.

Final results were expressed as % of decrease in number of viable microorganism on LB-agar plates with addition of specific carbon material compared with the control plate (only LB-agar). Two concentration of activated carbonaceous material were used – 1mg/ml and 3 mg/ml.

RESULTS AND DISCUSSION

Differences in texture of PTA and PTB samples are best observed by SEM analysis of samples (Figure 2a and b). PTAs are larger (Figure 2 a) and have relief texture compared to smooth PTBs (Figure 2 b). After HTCP texture of both samples were changed according to the severe experimental conditions. Influence of acid, temperature and pressure changed texture that became more relief than before HTCP. Presence of silver couldn’t be seen by this technique. It is expected because silver on the SEM micrographs can be seen only if it has special form – fibrous.

The presence of silver was observed by XRD analysis, (Figure 3). In all three cases the presence of mixture of XRD patterns of silver metal and silver (I) oxide was notified. But, clearly can be seen that silver is better settled on the bristles (Figure 3c), than on achene (Figure 3b), whether it is metal or oxide. Also, the XRD pattern of CPTB determines the XRD pattern of the entire sample CPTS.

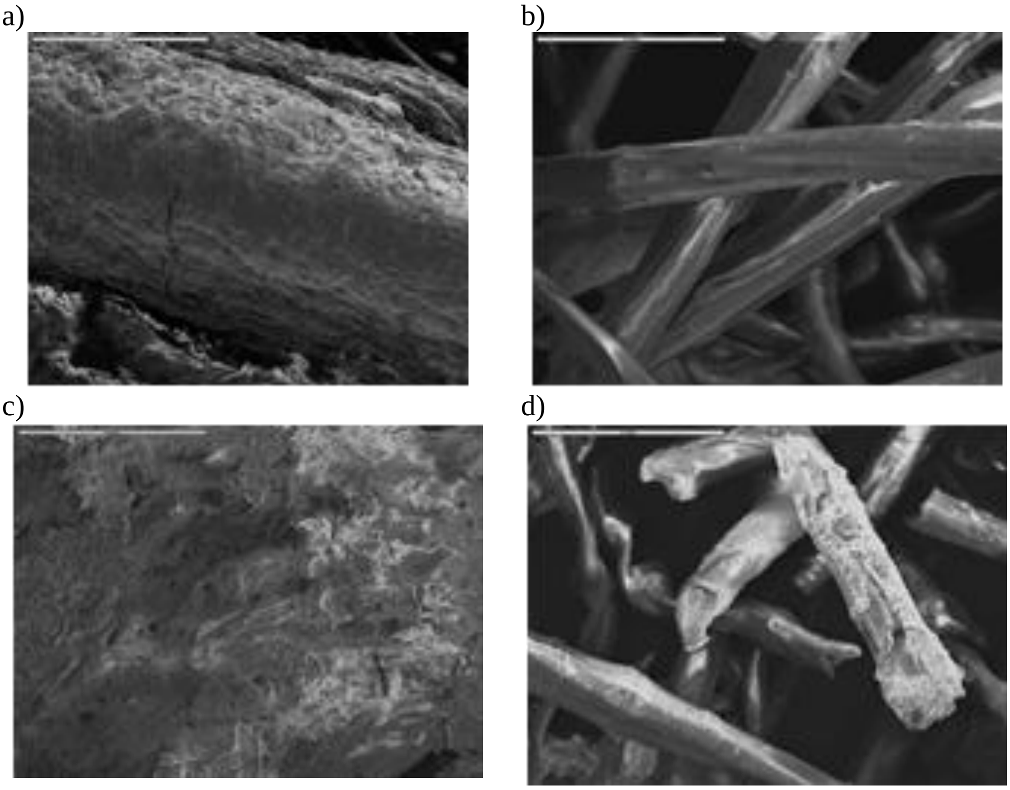

***Figure 2** SEM micrographs of raw material: a) achene – PTA and b) bristles – PTB, and after HTCP: c) CPTA; d) CPTB.*

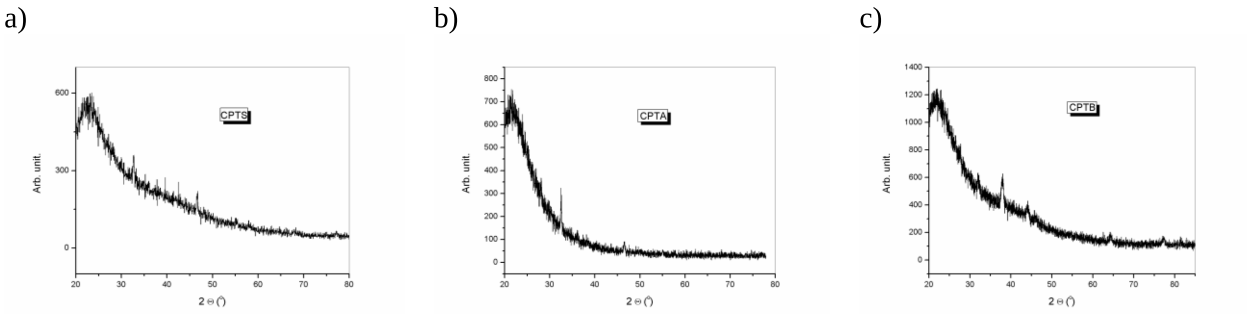

***Figure 3** XRD pattern of carbonized samples: a) CPTS, b) CPTA, and c) CPTB.*

Decrease in the number of colony forming units (d CFU) compared to the control plate, for both concentration (1 and 3 mg/ml) of carbonaceous material is shown in Table 1. All of these samples have shown remarkable traits in removing microbes found in a suitable environment (stream).

***Table 1** Decrease in the number of colony forming units (d CFU) compared to the control plate, for both concentrations*

Sample	d CFU (%) 1 mg/ml	d CFU (%) 3 mg/ml
CPTS	90	100
CPTA	100	100
CPTB	100	100

The reduction in microbial development was only in one case 90% (at a lower concentration of the CPTS sample) and in other cases 100%. The reason for this can be that silver oxide, which is deposited on carbonized material along with metal silver, is also an antimicrobial agent [20].

CONCLUSION

Both parts of plane tree seed – achene and bristles as well as whole seed, after hydrothermal carbonization process under given conditions, showed significant antimicrobial effects. Although bristles seems to be better for functionalization with silver metal and oxide, than achene, both samples 100 % decreased the number of colony forming units compared to the control plate, for both concentration 1 and 3 mg/ml.

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POSSIBILITIES FOR MANAGING THE CIGARETTE BUTTS WASTE

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Abstract

A major existing consequence of the use of tobacco products, such as filter-tipped and roll-your-own cigarettes, is the waste disposal of discarded cigarette filters or butts, which can long time persist in the environment. The literature review found that: 1) Cigarette butts can contain many of the chemicals found in cigarette smoke, and they harm the environment causing air, water, and soil pollution; 2) A number of studies have investigated the chemicals found in cigarette butts and their cumulative effect; 3) Numerous studies state that cellulose acetate is not biodegradable, pointing to its extremely slow rate of degradation. The goal of this study is to assess the potential ecological risks of cigarette butts waste to the environment in some of the Balkan countries and create public awareness about its toxicity. Knowledge about the toxicity of cigarette butts to the environment will aid in understanding the environmental load of cigarette butt litter. Consequently, regulatory policies and approaches to removing cigarette butt waste could be better justified and designed. Approaches can include anti-butts messages on cigarette packaging and advertisements, distribution of small, free portable ashtrays, and placement and maintenance of conspicuous ashtrays in areas where smokers gather. Cigarette manufacturers need to take an active and responsible role in educating smokers about this issue and devote resources to the cleanup of cigarette butts.

Keywords: Environment, Pollutant, Cigarette butts, Chemicals, Smokers

INTRODUCTION

Globally, smoking prevalence - the percentage of the population that smokes cigarettes has decreased, but the number of smokers worldwide has increased due to population growth. Machine manufactured cigarettes are the most commonly used form of tobacco, accounting for 92.3% of tobacco product sales worldwide, and most of them are filter-tipped [1]. However, there is another very popular smoking product cheaper than commercial cigarettes a roll-your-own (RYO) cigarette. With a 1 billion smokers in 2014 consuming an estimated 6.25 trillion cigarettes worldwide and nine trillion expected by 2025, the global environmental load of cigarette waste is significant [1,2].

Many smokers who do not properly dispose of their extinguished filters, partially-smoked cigarettes, lighting material, and packaging do not consider their behavior littering [3]. The problem has increased in recent years because many of governments brought legislation for smoking restrictions in public buildings and restaurants forcing smokers outside, where butts are often littered.

More than 6 trillion cigarettes are smoked worldwide each year, and all of them are disposed of in some manner. They are dropped on the ground, tossed in trash bins and carted off to landfills. Regardless of how the butts are disposed of today, each one of them may pose a toxic hazard to the environment. Therefore it is very important to properly manage this toxic waste [4,5].

In discarded cigarette butts, many chemicals may be found that are sourced from agricultural treatments of tobacco plants, uptake from contaminated soils, additives used in the manufacturing process, the attached cellulose acetate filter, and combustion products generated in the process of smoking cigarettes [5,6].

The impact that tobacco has on the environment is less well recognized. The World Health Organization (WHO) and Framework Convention on Tobacco Control (FCTC) address the environmental concerns regarding tobacco in Article 18. Both cigarettes smoke itself and butts as the post-consumption waste from cigarettes represent potential point sources for environmental contamination. Republic of Macedonia, Serbia, Bulgaria, and Bosnia and Herzegovina have all ratified the WHO Framework Convention on Tobacco Control (WHO FCTC). Despite the decline of tobacco smoking prevalence over the past decades all four countries have one of the highest smoking prevalence among adults in comparison with European countries.

The conducted research should help in realizing the state of the cigarette waste management in the Macedonia, Serbia, Bulgaria, and Bosnia and Herzegovina. The situation in this countries and the comparison with the countries of the European Union in the field of cigarette waste management and treatment options are presented.

The goal of this study is to assess the potential ecological risks of cigarette butts waste to the environment in some of the Balkan countries and create public awareness about its toxicity.

DISCUSSION

To get important background information and knowledge about the field of research, study material about cigarette butt litter, and its impact on the environment, legislation and responsibilities towards environment; we accessed books, scientific articles, journals, and other reliable websites active in the field.

As a result of new legislation concerning marketing restrictions and plain packaging, filters are one of the few components left for cigarette manufacturers to utilize to differentiate themselves and communicate to the consumer using different sizes, shapes and colors.

Cigarette manufacturers are contemplating and test marketing additional “reduced harm” cigarette filter, including new types of filters that may reduce toxic constituents in cigarette smoke or design approaches. The cigarette manufacturers have been concerned that aesthetic and environmental concerns related to cigarette butts could contribute to the growing social unacceptability of smoking and regulation that manufacturers are responsible for butt disposal. About 99% of the manufactured cigarette market is filtered cigarettes; filters degrade very slowly and thus become an accumulating mass of potentially toxic waste.

Many smokers do not properly dispose of their extinguished filters even when appropriate waste receptacles were available, they still discarded their tobacco product waste into the environment. Discarded cigarette butts consist of three components: remnant tobacco (including partially smoked/charred tobacco on the end), the filter and a paper wrap. Each of these components of the discarded cigarette butt presents its own concerns.

Discarded cigarette butts contain various chemicals, nicotine, pesticides and carcinogens found in cigarettes, and can contaminate the environment and water sources. These chemicals are sourced from agricultural treatments of tobacco plants, uptake from contaminated soils, additives instilled in the manufacturing process, and combustion products generated in the course of smoking cigarettes [7-9].

Toxic substances are leached from butts that pollute waterways, and probably pollute ground water near landfills that are not properly constructed to contain such leachates. Butts collect in municipal storm drains and then may empty into waterways. Because of the volume they can achieve, they can block storm drains and sanitary sewer systems. Aquatic life may be harmed by the toxic leachates, and the butts may cause physical harm when ingested by animals.

At the top of the cigarette waste management hierarchy, prevention and minimization of waste generation, which represent the most acceptable options from the point of view of environmental protection, because their use reduces the total quantity and hazardous characteristics of this type of waste.

Balkan countries are a major target for tobacco industry sales and marketing. Also, many tobacco companies now located their manufacturing plants in Balkans. Despite the decline of tobacco smoking prevalence over the past decade (2000-2015) all four countries have one of the highest smoking consumption in comparison with European countries [1,10].

Table 1 *The rate of cigarette consumption (2000-2015)*

Country	Rate 2000	Rate 2015	Absolute changes between 2015-2000	Percentage change between 2000-2015
Bosnia and Herzegovina	46.8	38.6	-8.2	-18
Bulgaria	50.4	35.3	-15.1	-30
Macedonia	37.9	33.7	-4.2	-11
Serbia	47.9	41.5	-6.25	-13

This Table 1 displays the rate of cigarette consumption in 2000 and 2015. There are significant and persistent differences in the prevalence of smoking, with the highest rates observed in Bulgaria. The lowest proportions are found in Serbia and Bosnia and Herzegovina. The percentage change between consumption in 2000 and 2015 was noticeable in the case of Bulgaria.

It is well-known that waste management is not only a technical issue, but largely depends on various factors such as politics, legislation, sociological and cultural factors and economics. The aforementioned factors interconnected make the waste management process more difficult.

A search of online resources, including news clippings and local publications revealed that the Republic of Macedonia, Serbia, Bulgaria, and Bosnia and Herzegovina have not attempted to implement legislation to specifically designate cigarettes as litter (Table 2).

Table 2 *Overview of countries in waste management activities*

Country	Current Law	City and Municipality	Fine	Legislation relate to cigarette waste
Bosnia and Herzegovina	Law of Waste Management Waste Management Strategy	Waste Management Plan (for a period of 5 years)	Generally 50 BAM	None found
Bulgaria	Law of Waste Management Waste Management Strategy	Each city adopts a Waste Management Ordinance, transcribing the law and upgrading the fine. Waste Management Program (for a period of 5 years)	The Municipality of Plovdiv has imposed a fine of 50 BGN, although it has registered between 10 and 50 in the Ordinance.	None found
Macedonia	The Law of Waste Management Law of Public Cleansing Waste Management Strategy	Waste Management Program (for a period of 5 years)	Generally 3000 MKD	None found
Serbia	The Law of Waste Management Law of Public Cleansing Waste Management Strategy	Waste Management Strategy Waste Management Plan (for a period of 5 years)	The Beograd Municipality has imposed a fine of 10000RSD. Decision to maintain cleanliness	None found

From the data shown in Table 2 we concluded that all countries have implemented national state laws. The Waste Management Policy is defined in the Waste Management Strategy of each country. In general, the Strategies define short-term and medium-term municipal waste management objectives. It also includes the target date for 2020 or 2015. The Law on Waste Management is a key law that has introduced the concept of local and regional plans for 5 year planning. These State laws include a variety of litter and dumping ordinances but no pending legislative proposals for cigarette waste could be identified in all countries. The responsibility for cleaning up cigarette product waste falls to municipalities, local communities and the governments using taxpayer funding. Municipalities today devote significant time and money to cleaning public areas and removing litter, including cigarette waste.

City administrations in all four countries do not give enough attention to cigarette waste management. The main reasons are limited and insufficient resources and no understanding of the factors that influence the different levels of toxic waste management. As a result, there is a low level of quality of services necessary for the protection of public health and the environment.

The current situation in the municipalities of all countries has characterized up to now unreliable and incomplete data on the amount and composition of municipal waste. There is no data on the share of cigarettes waste in the total quantity of waste.

European Union EU waste policy aims to make waste management more efficient for the Union as a whole by managing waste as a resource and moving towards a European recycling society in which Member States can develop self-sufficient waste disposal systems. Waste policies and targets set at the level EU include minimum requirements for managing certain waste types. The most relevant targets for municipal waste are the Landfill Directive’s [11] landfill diversion targets for biodegradable municipal waste; the Packaging and Packaging Waste Directive’s [12] recycling targets; and the Waste Framework Directive’s [13] target on recycling and preparing for reuse. Countries can choose between four different methods to monitor their progress towards the last target [14]. There is a third level of legislation, with seven specific laws that deal with different waste streams: sewage sludge in agriculture; packaging and packaging waste; PCBs/PCTs; end-of-life vehicles; batteries and accumulators; restriction of hazardous substances in electrical and electronic equipment (RoHS 2); and waste electrical and electronic equipment.

Republic of Bulgaria as member of European Union Bulgaria submits the Operational Programme Environment 2014-2020. With the implementation of programme is expected to contribute to sustainable municipal waste management, according to the waste management hierarchy without planning the management of waste from cigarettes.

Republic of Macedonia, Serbia and Bosnia and Herzegovina are developing countries, and as such have to pay particular attention to improving the waste management system including cigarette butt waste, as one of the key elements of environmental protection. Therefore, a good basis should be established, in order to further develop the waste management system in the future. Environmental protection is the goal that the countries are striving for improvement the integration process to EU legislation.

These activities should be carried out at the level of local communities and the municipality, and then at the city level. While local initiatives carry the full force of state law, research shows that they serve to unite communities behind the waste target.

Based on the information from the available literature there are several strategies to reduce or eliminate the public health and environmental effects of cigarette butt waste have focused on following methods: 1) making cigarette butt waste less toxic and persistent, 2) consumer education and responsibility to reducing the number of discarded cigarettes butts and 3) extended cigarette manufacturers responsibility. Approaches can include anti-butts messages on cigarette packaging and advertisements, distribution of small, free portable ashtrays, and placement and maintenance of conspicuous ashtrays in areas where smokers gather. Cigarette manufacturers need to take an active and responsible role in educating smokers about this issue and devote resources to the cleanup of cigarette butts.

CONCLUSION

Butt litter as an environmental and public health hazard is a relatively new field of study, but recent research and findings provided evidence for the slow degradability of cigarette filters and the harmful presence of their chemicals in the environment.

The determination of the quantity of cigarette waste, the adoption of these results and their designation by the national institution is of crucial importance for effective municipal waste management.

State laws include a variety of litter and dumping ordinances but it is important Macedonia, Serbia, Bulgaria, and Bosnia and Herzegovina should attempted to implement legislation to specifically designate cigarettes as waste.

Several options are available to reduce the environmental impact of cigarette butt waste, including developing biodegradable filters, increasing fines and penalties for littering butts, monetary deposits on filters, increasing availability of butt receptacles, and expanded public education.

Potential responses to cigarette butt waste include anti-butts messages on all packaging and advertisements, distribution of small, free portable ashtrays, and placement and maintenance of outdoor ashtrays in areas where smokers gather.

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PROCEDURE FOR MANAGEMENT OF SELF-CONTAINED SELF-RESCUER AS A WASTE IN UNDERGROUND COAL MINING

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Abstract

In underground coal mines, there is a possibility to the generation of unfavourable working environment conditions such is appearing of toxic gases. For this reason the legislator prescribed obligatory use of personal protective devices for the protection of respiratory organs - self-contained self-rescuer. The obligation of everyday wearing is prescribed for all workers who work in the underground coal mines, so a large number of self-contained self-rescuer units accumulate on the mines. After the expiry date, these self-rescuer need to be treated further. The question arises: how to manage these self-rescuer? According to the current legislation on waste management, "waste is any matter or object that the holder discards, intends or is required to discard." However, for insulating self-rescuer used in mines, the manufacturer has prescribed a procedure that implies scaling, neutralization and, after the neutralization process in the form of non-hazardous waste, is handed over to the certified operator. The procedure itself consists of several independent procedures that are described in this paper and discussed their compliance with the current legislation in the RS.

Keywords: Self-rescuer, Waste, Procedure

INTRODUCTION

The Waste Management Act prescribes procedures related to the collection, storage and management of waste [1]. The waste management procedure is an obligation for all employers. In underground mines, due to the specificity of technology, during the introduction of these procedures in the course and everyday work encounters new problems. One of these specificities is also related to the treatment insulating self-rescuers as a waste. Self-rescuers in the regenerative cartridge contain toxic substances that can be hazardous to the living and working environment. In addition to being able to cause environmental pollution, they can lead to ignition of plastic, wood or other flammable substances. The manufacturer is in the technical manual of the self-rescuers prescribed a method for neutralization of the cartridge with the active substance after the expiry.

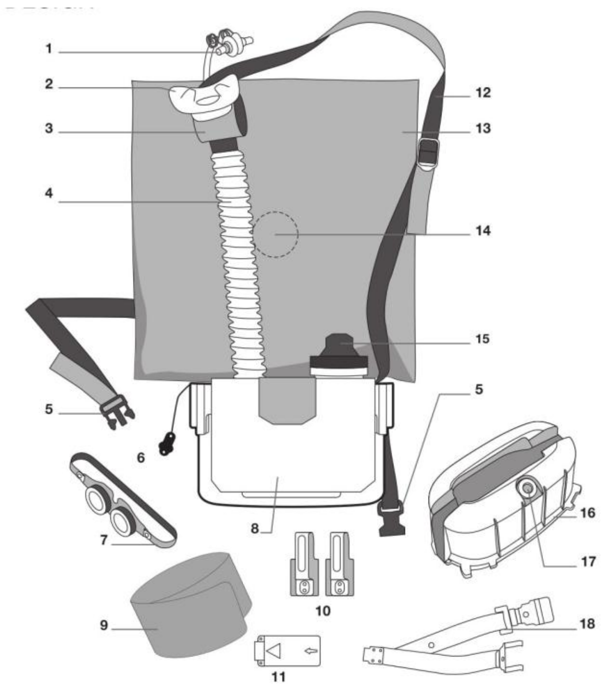
The main problem is in which way this type of waste should be treats, according to Waste management act or by producer guidelines.

INSULATING SELF-RESCUERS CI-30KS

Self-rescuers CI-30KS, shown on Figure 1, is a protective device for respiratory organs from harmful and toxic gases (CO, CO_2, H_2S, NO_x gases). It is used for exit of workers from working environment endangered by harmful and toxic gases and smoky areas or from an environment with insufficient of oxygen, in a ventilation facilities with fresh air, [2]. Self-rescuers which are used in mines must comply with the SRPS EN 13794: 2008 standard and the Rulebook on Personal Protective Equipment [3,4]. They must also have an Expert Test Finding made by an Authorized Institution in which the Examiner determines whether all requirements, relating to the Standard and the Rulebook, for the guaranteed term of 5 years have been met [5].

Workers who perform their work in underground coal mines have obligation to have a self-rescuers during the every shifts, which is prescribed by the regulatory act, [6]. Before carrying self-rescuers each worker has to visually checks of the self-rescuers, whether the metal rim is damaged and hermetic closed and that they are no cracks on the box. On the self-rescuer there is a blue indicator that will change colour if the self-rescuer is no longer hermetically sealed.

After the expiry date, a large number of unused self-rescuers devices are accumulated, and they should be treated as waste. Except for reactive cartridges, all other parts can be treated as non-hazardous waste. Figure 1 shows of the components of the self-rescuer.



Ci-30 consists of the following elements:

1. Nose clip	7. Goggles	13. Breathing bag
2. Mouthpiece	8. Heat shield	14. Relief valve
3. Heat exchanger	9. Rim	15. Starter
4. Breathing hose	10. Belt loops	16. Lid
5. Chest strap	11. Cover plate	17. Moisture indicator
6. Mouthpiece plug	12. Neck strap	18. Coupling strap

Figure 1 *Elements of the self-rescuer CI 30KS [7]*

Reactive potassium cartridge (reactive cartridge) on Figure 1, position 8, is used to create oxygen using carbon dioxide from the breath according to following reaction:

$$4KO_2+CO_2+H_2O \rightarrow K_2CO_3+2KOH+3O_2 \quad (1)$$

$$KOH+CO_2 \rightarrow KHCO_3 \quad (2)$$

POSSIBILITY FOR DISPOSING OF SELF-RESCUERS AS WASTE

There are two possibilities for disposing of the self-rescuers after expiry date. The first one is according to producer procedure and second is according to waste management act.

Producer procedure

Used self-rescuers, expired, as well as self-rescuers unfit for further use, must be disposed of. Disposal process is following [7]:

1. Open self-rescuer;
2. Manually actuate the starter;
3. Disconnect hose and breathing bag;
4. Remove the cartridge from the casing;
5. Place cartridge in clean water with tubes up and keep it there, shaking slightly until bubbles stop to appear;
6. Neutralize the alkaline solution produced with 3% acid, for example, hydrochloric acid (HCl);
7. Sort out all the details and components by type of material (metal, plastic, resin, etc.) and dispose of in accordance with the regulations applicable in your territory;
8. Record the disposal in the self-rescuer register. Use safety glasses and gloves during disposal procedure.

Waste management act

Contrary to the manufacturer's instructions Waste Management Act describes how to storage, storage and disposal of waste and the numerous of clauses are contrary to the manufacturer's instructions. According to Waste Management Act (clause 44), the production, collection and transport of hazardous waste, as well as its storage and treatment, shall be carried out under conditions that ensure the protection of the environment and human health in accordance with clause 3 of this Act, including all activities from production to treatment of hazardous waste, in accordance with the reporting on waste, supervision and penal provisions in the manner prescribed by this Act. Treatment of hazardous waste has priority in relation to other waste treatment and is done only in plants that have a permit for the treatment of hazardous waste in accordance with this Act.

During the hazardous waste collecting, sorting, storing, transporting, reusing and disposing, hazardous waste is packaged and labelled in a way that ensures safety for human health and the environment, in accordance with international and harmonized Serbian standards.

It is forbidden to mix different categories of hazardous waste or to mix hazardous waste with non-hazardous waste, other substances and materials, except:

1) in a plants for which the license was issued for the treatment of hazardous waste in accordance with clause 64 of the Act;

2) if clause 3 of this Act is applied and does not come to the harmful effects of waste management on human health and the environment;

3) under the conditions specified in the license with the use of the best available techniques and under the supervision of qualified persons.

Dispose of hazardous waste without prior treatment which significantly would be reduce hazardous waste characteristics is forbidden. Dilute of hazardous waste in goal to discharge into the environment is forbidden also.

As can be concluded from the aforementioned clauses of the A, our legal regulations strictly prohibit the mixing or dilution of hazardous substances, as well as the discharge of this solution into the environment.

RESULTS OF THE SELF-RESCURER CARIDGE TREATMENT

The basic component of potassium cartridge, that provides breathing using self-rescuer, is potassium superoxide. Potassium cartridge is shown on Figure 2.

Figure 2 *Potassium cartridge of CI -30KS self-rescuer*

In order to analyse the proper treatment of waste solutions obtained by dissolving the potassium cartridge of self-isolation rescuer CI-30 HP in water in laboratory conditions according to the manufacturer's instructions. In the manufacturer guidance there no instructions are given on the quantity of water required to dissolute the potassium cartridge. Because of that three samples were analysed, solution with a weight of 5%, 10% and 20% potassium superoxide. That means, in practice for a one self-rescuer it is necessary to use 11.4 l of water for 5% potassium superoxide in solution, 5.4 l of water for 10% potassium superoxide in solution and 2.4 l of water for 20% potassium superoxide in solution. By dissolving patrons in water, a very basic solution is obtained. It is necessary to neutralize it. Three acids, that can be found in wide consumption, to neutralize the solution were used: hydrochloric acid (HCl), acetic acid (CH_3COOH) and citric acid ($C_6H_8O_7$).

Table 1 *Analysis of the pH of the neutralized solution of potassium superoxide*

Mass content of KO_2 in solution	Type of acid	Mass content of acid in solution	pH value
5%	HCl	3%	12.92
10%	HCl	3%	13.70
5%	CH_3COOH	3%	13.27
10%	CH_3COOH	3%	13.96
5%	$C_6H_8O_7$	3%	13.61
10%	$C_6H_8O_7$	3%	13.98
20%	$C_6H_8O_7$	3%	14.33

As can be seen in Table 1, the recommended acidity of 3% of the weight required for the neutralization of the potassium superoxide cartridge solution is not sufficient, since after treatment, the very basic solution remained approximately the same pH value.

For the more precise determination of the amount of acid needed to add to the solution to neutralize, a solution of 5% and 10% potassium superoxide test was performed with HCl and the following graph was obtained (Figure 3).

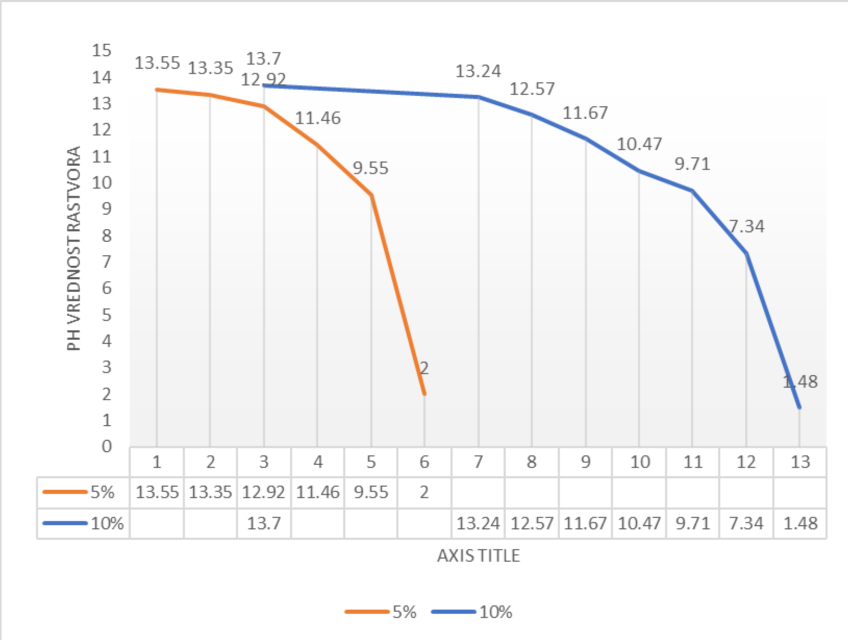


Figure 3 *Results of acid amount test*

A greater amount of acid is required to neutralize high basic solutions, for 5% solution 5.1% of acid is needed and for 10% solution 12.05% of acid is needed.

CONCLUSION

Laboratory analyses have shown that 11.4 liters of water is needed for the dissolution of one potassium cartridge. There also has been determined that there is no complete dissolution and that the solution has a chemical residue. Beside that a great amount of acid is needed for neutralize high basic solution. Thus, independent treatment of self-rescuer cartridge according to the manufacturer's instructions does not provide a harmless substance that can be dropped into the environment without polluting.

According to facts mentioned above can conclude that waste self-rescuer should be treated as hazardous waste. As a first it is necessary to examine what types of hazardous material is contained in the cartridge at the authorized laboratory. After determining the type of waste it is necessary to properly dispose. After that it should be stored and kept on for at least one year and after the expiration of this deadline, it will be handed over to an authorized operator for further treatment.

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ADSORPTION OF Cr^{3+} FROM AQUEOUS SOLUTION USING BENTONITE CLAY COMPOSITE

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Abstract

Fast industrialization and urbanization of cities has increased a degree of environmental pollution. Surface and underground waters are directly or indirectly threatened by higher volume of industrial wastewaters which are released without proper treatment for heavy metal removal. Chromium(III) (Cr^{3+}) in water and soil often comes from tannery, chemical industry as well as cellulose and paper industry wastewater. In this paper, we investigated the possibility of using bentonite clay composite for Cr^{3+} removal from synthetic aqueous solutions. The optimal parameters for the adsorption process were determined and the sorption process is endothermic, as suggested by the value of adsorption enthalpy.

Keywords: Cr^{3+}, Adsorption, Bentonite clay, Enthalpy

INTRODUCTION

Chromium metal has three stable valence states, i.e. 0, +3 and +6 [1]. Depending on the source (type of industry), in the wastewater, chromium can have the form of hydrated ions $[Cr(H_2O)_6]^{3+}$ (galvanic wastes) or complex neutral, anionic or cationic compounds (textile dyeing waste). Depending on pH, Cr(III) occurs as soluble Cr^{3+} and $CrOH_2^+$, $Cr(OH)^{2+}$, $Cr(OH)_3$, or as $Cr(OH)^-_4$ ions in aqueous solutions [2].

Cr^{3+} is an essential trace mineral. It has an important role in the metabolism of lipids, carbohydrates and proteins [3,4]. Likewise, it has toxic effects. Eastmond *et al.* [5] in their paper state that even Cr^{3+}, when taken as a supplement, can be accumulated in tissues and can bring about structural changes in DNA. International environmental standards require that Cr^{3+} in wastewater should not exceed 5 mg/L [6].

Many methods were employed for Cr^{3+} removal from wastewaters. Most significant among them were: surface adsorption, chemical precipitation, electrolysis, membrane filtration, ion exchange, foam flotation etc. [7-9]. Adsorption is a process for removal of heavy metals that receives attention since it is easy to implement and because of its economic and efficiency advantages.

In this study, bentonite clay composite was used as an adsorbent for the removal of Cr^{3+} from aqueous solutions. The major aim was to test the performance of bentonite clay composite in the function of the adsorbent dose, pH and temperature.

MATERIALS AND METHODS

All reagents used in this study were of analytical grade. Stock solutions of Cr^{3+} were prepared by dissolving chromium(III)chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) in double distilled water. Analytical solutions were prepared by dilution of the stock solution and, when needed, pH was adjusted to the desired value by addition of either 1 M HCl or 1 M NaOH. The stirring speed was constant and fixed at 400 rpm during the test at room temperature (20°C). The experiments were terminated at a contact time of 25 min. The clay used was bentonite produced by Riznica Prirode from Serbia. Clay contains: montmorillonite, kaolinite, illite and muscovite. The chemical composition of montmorillonite is presented in Table 1.

***Table 1** The chemical composition of montmorillonite*

Compound	SiO_2	Al_2O_3	K_2O	Fe_2O_3	TiO_2	MgO	CaO
Amount (wt.%)	68.05	24.45	3.51	1.70	1.09	0.68	0.52

Solution's pH was measured using pH-EC-TDS meter, HI 9812, Hanna instruments. At the end of each adsorption period, the adsorbents were filtered through filter paper (Blue ribbon, Chmlab) and the residual Cr^{3+} concentration was analyzed by an Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES) (Optima 8300, Perkin Elmer, USA).

The removal percentage of (R%) Cr^{3+} ions by clay minerals and the adsorption capacity q_e (mg/g) after equilibrium was calculated by equations as follows:

$$R(\%) = \frac{Ci - Ce}{Ci} \cdot 100 \tag{1}$$

$$q_e = \frac{Ci - Ce}{m} \cdot V \tag{2}$$

where:

C_i is the initial concentration of metal ions in the solution (mg/dm^3),

C_e is the final concentration of metal ions in the solution (mg/dm^3),

V is the volume of the solution (dm^3),

m is the mass of the adsorbent (g).

RESULTS AND DISCUSSION

Adsorption Experiments

Effect of the adsorbent dosage

Effect of the adsorbent dosage on adsorption coefficient of Cr^{3+} from aqueous solutions is obtained by varying mass of clay in an interval from 0.14 to 5 g. Experiments were carried out on room temperature with 50 ml of 157 mg/L Cr^{3+} solution. Starting pH of the suspension was 4.5. Concentration of Cr^{3+} was measured after 25 min and was graphed in Figure 1. From Figure 1 it can be concluded that removal coefficient of chromium increases with the increase of concentration of solids. Khan *et al.* [10] concluded that the increase of adsorption coefficient with an increase of adsorbent concentration can be caused by an increase of total free surface of the adsorbent. Moreover, the inverse proportion was observed for adsorption capacity. The decrease in adsorption capacity was attributed to the splitting effect of the concentration gradient between sorbate and sorbent with increased bentonite clay composite dosage, leading to a decrease in the amount of Cr^{3+} over a sorbent unit weight [11].

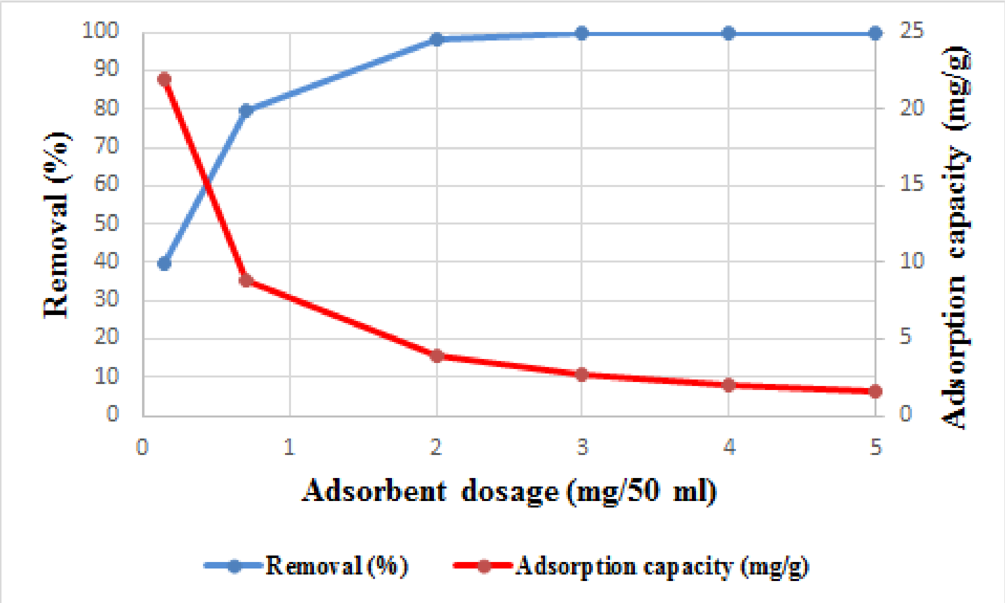

***Figure 1** Effect of slurry concentration on adsorption of Cr^{3+} by bentonite*

Effect of pH

In order to investigate the influence of the solution's pH on the adsorption of chromium on bentonite, a series of solutions with the following pH values were made: 0.9, 4.5, 7.5, 11.4 and 13. In a 150 ml beaker, 1 g of clay was measured, and a 50 ml of the Cr^{3+} solution of exactly known concentration (157 mg/L) was added. The pH value of 4.5 was adjusted by adding HCl and NaOH. The reaction mixture was stirred for 25 min. The obtained results are shown in Figure 2.

From Figure 2 it can be seen that the degree of chromium removal increases with a rise in pH in the range of 0.9–14. Over pH 7.5, it reaches a plateau. When performing experiments, high pH values should be avoided, because the precipitation process may occur and hinder the distinction between adsorption and precipitation as a main metal removal process. Also, in our experiment, we observed a change in the color shade of the solution around pH 3.6 which corresponds to the change from Cr^{3+} to $Cr(OH)^{2+}$. Chen *et al.* [12] in their paper point out that the great influence of pH on the adsorption degree indicates that adsorption is dominated by surface complexation which is in accordance with the surface complexation model. Thus, the authors believe that the adsorption of Cr^{3+} can be attributed to the ion exchange between Cr^{3+} and H^+/Na^+ on the ion exchange sites at low pH values. At pH > 5, the Cr^{3+} will precipitate from solution.

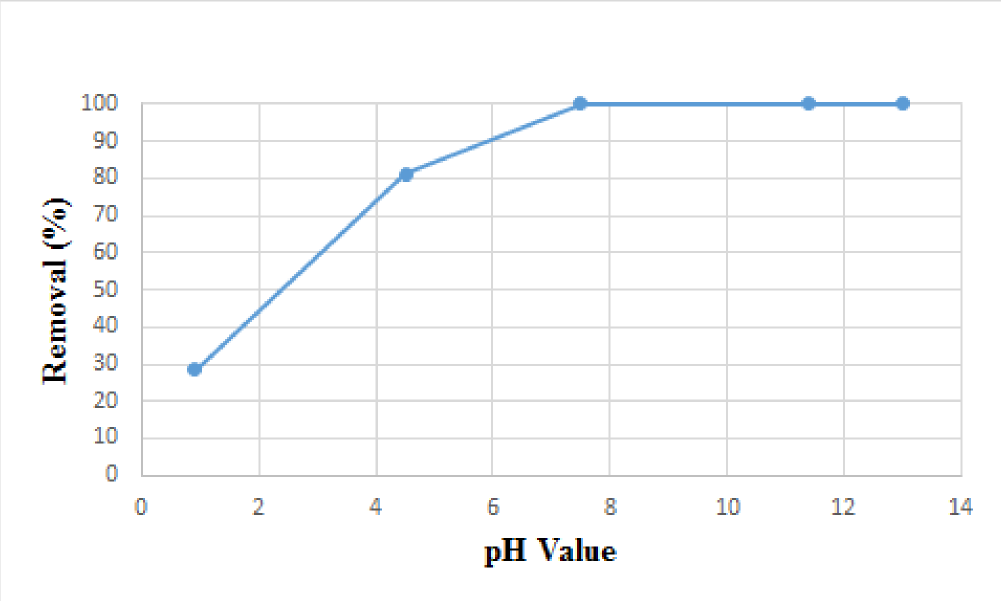

Figure 2 *Effect of initial pH on adsorption of Cr^{3+} by bentonite*

Effect of temperature on adsorption

The influence of temperature on the degree of chromium removal from aqueous solutions was tested at temperatures of 20, 35, 50, 65 and 80 ºC. In a 150 ml beaker, 1 g of clay sample was weighed and a 50 ml of the Cr^{3+} solution of exactly known concentration (157 mg/dm^3) was added at a pH 4.5. Suspension was mixed for 25 min on a magnetic stirrer with heating. The first sample was not heated, because it was equivalent to room temperature. Each subsequent sample was heated on a water bath. The obtained results are shown in Figure 3.

Based on the results presented in Figure 3, it can be concluded that the degree of removal of Cr^{3+} increases with the increase in the solution temperature. Similar results have been obtained in Chen *et al*. [12] and Tahir and Naseem [13] works. According to Clausius-Clapeyron equation [12]:

$$H = R \cdot \left[\frac{d(lnCe)}{d(1/T)} \right] \tag{3}$$

where:

R is the molar gas constant (8.314 J/molK),

T is the absolute temperature (K).

By integration of (3), the following can be obtained:

$$\log C_e = \frac{\Delta H}{2.303RT} + \frac{1}{T} + b \tag{4}$$

where b is constant.

Plotting $\log C_e$ against 1/T gave a straight line with a slope equal to ΔH/2.303R. The enthalpy of adsorption was calculated to be 2.489 kJ/mol. The positive value of ΔH confirmed the endothermic nature of the adsorption process. Tahir and Naseem [13] believe that one possible explanation why adsorption is endothermic is that metal ions are well solvated in aqueous solutions. In order for the metal ions to be adsorbed, they have to lose part of their hydration sheath. This dehydration process of the ions requires energy. Authors assume that this energy of dehydration supersedes the exothermicity of the ions getting attached to the surface. The implicit assumption here is that on adsorption, the environment of the metal ions is less aqueous than in its dissolved state.

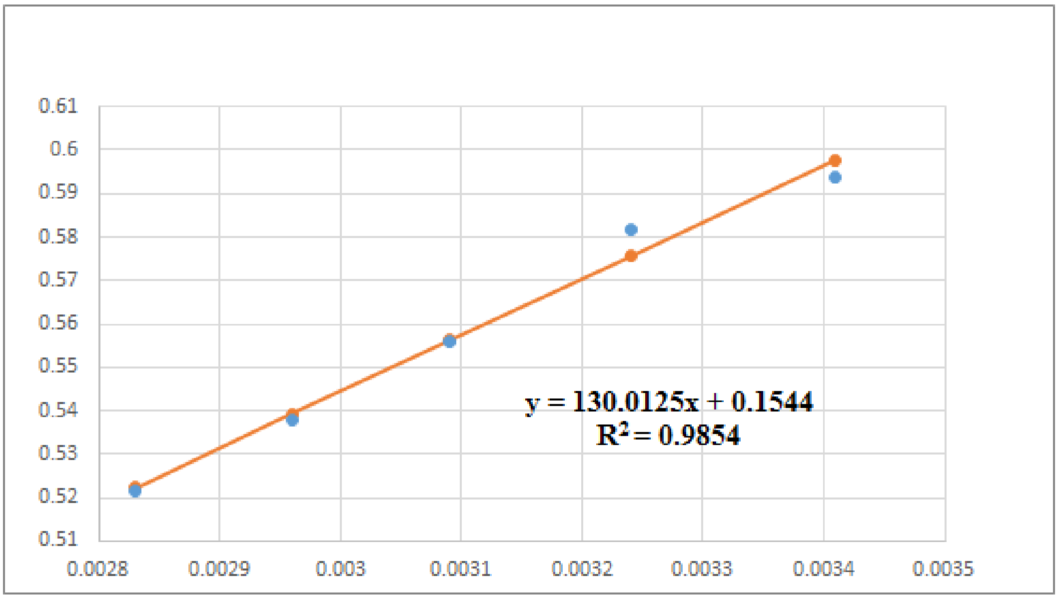

Figure 3 *Effect of temperature on adsorption of Cr^{3+} by bentonite*

CONCLUSION

It can be concluded on the basis of literature data, analysis and discussions of obtained experimental results, that:

- Bentonite clay composite is an effective natural material for Cr^{3+} removal from industrial wastewater.
- Adsorption capacity of studied clay depends on the mass of adsorbent, temperature, and pH of aqueous solutions.
- At pH 3.6 hydroxyl complex of chromium $Cr(OH)^{2+}$ is formed and at pH 5 hydroxide $Cr(OH)_3$ is formed.
- Enthalpy of 2.489 kJ/mol suggests that the process is endothermic.

ACKNOWLEDGEMENT

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ECOLOGICAL-HYGIENIC APPROACH TO THE ASSESSMENT ON THE HEALTH OF THE POPULATION OF BELARUS

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Abstract

Based on the analysis of numerous data, it was found that when small doses of industrial toxicants are applied, the initial reaction of the organism manifests itself in the stimulation of protective mechanisms, which at the first stage does not affect the overall morbidity level. In the future, with prolonged exposure to chemical contaminants, the incidence may increase spasmodically. With the inclusion of adaptation and resistance mechanisms, morbidity rates may again return to the previous level, after which the next uptake will occur. It is shown that the use of the risk assessment method is preferable and gives the best results for estimating the expected adverse effect of polluting chemicals on public health.

Keywords: Environmental medicine, Industrial pollution, Etiology of diseases, Environmental assessment, Medical-geographical zoning

INTRODUCTION

The impact of pollutant chemicals in the atmosphere is multi-vector. The direct effects of atmospheric pollutants on humans, animals, plants and soil can affect the structure and functioning of natural ecosystems, including their ability to self-regulate. In addition, the sedimentation of atmospheric pollutants on environmental objects and their absorption by plants and animals leads to the penetration of chemicals into drinking water, food chains, and therefore serves as an additional source of human exposure, health, and also affects the quality of life [1-4].

Numerous literature data of both domestic and foreign authors show that air pollution by chemical substances has a negative impact on the population health. In recent years, the terms "eco-illness", "multiple chemical susceptibility syndrome", "environmental intoxication" according to the WHO definition is a "disease caused by the environment" [4].

A number of studies has proved the impact of emissions from certain industries on human health. It is shown that the etiology of almost all groups of diseases in the population of industrial cities - the pathology of the reproductive system and diseases of newborns, respiratory diseases, the nervous system, allergic and autoimmune diseases, neoplasms, blood diseases, and cardiovascular system are associated with increasing pollution of atmospheric air. Studying the changes in the health status of the population under the influence of environmental factors, there were observed and described the following immunomodulatory effects: transient inhibition and stimulation of the immune response, a shift in antibody peak, a decrease in avidity of antibodies, a change in the expression of surface cellular receptors, proliferative activity or differentiation of immunocompetent cells [5-9]. Based on the above, we attempted to assess the impact of environmental factors of the territory of the Republic of Belarus on the health of the country's population.

MATERIALS AND METHODS

The search for methodological approaches to the solution of these problems made it possible to identify a general line in research strategies on this problem in the form of regime observations of the state of certain biosphere components within the framework of European environmental monitoring and health status of the population of the Republic of Belarus.

As a result of materials generalization of long-term comprehensive in-house studies of the natural environment state of Belarus, based on the indication of man-made pollution using abiotic and biotic components, an indirect assessment of the patterns of ecological situation formation in the country under the influence of anthropogenic factors was performed. The risk assessment we propose to evaluate the expected adverse effects of polluting chemicals on public health is preferable and gives the best results.

RESULTS AND DISCUSSION

Until recently, the most common method for studying the effect of atmospheric pollutants on the population health status was the study and analysis of the incidence by classes of diseases caused by the effects of polluting chemicals. The analysis of publications devoted to the study of the health status of the population living in areas with a degree of atmospheric air pollution above the permissible level indicates the selective effect of certain chemicals on individual organs and systems. Thus, the inhalation of mercury vapors and its salts, monohydric alcohols, formaldehyde, toxic effects on the central nervous system, benzene, lead, and gasoline have the same effect for prolonged contact. In this case, there are neuropsychiatric disorders, dizziness, headaches, as well as memory decreases, speech becomes frustrated, stiffness appears, general inhibition.

The excessive accumulation of manganese in the body also affects the functioning of the central nervous system. This is manifested in fatigue, drowsiness, deterioration of memory functions. Since manganese is a polytropic poison, lungs, cardiovascular and hepatobiliary systems can be affected simultaneously, immune response is violated, mutagenic effects are noted. Increased concentrations of nitrogen dioxide in the inspired air, in addition to directing the effect on the respiratory system, enhances the action of carcinogenic substances, contributing to the occurrence of malignant tumors. Influencing the human body, nitrogen dioxide causes oxygen starvation of tissues, especially in children, changes in blood composition [4,10].

Anemia and damage to the blood system causes chronic effects of lead, cadmium. It is established that heavy metals stimulate the development of allergic reactions, as well as a direct relationship between allergy to the chromium and the pathology of the digestive system. Irritant effect on the upper respiratory tract and lungs is nitrogen dioxide, ammonia. Chronic intoxication with nickel, iron leads to the occurrence of diseases of the nasopharynx, lungs. Ammonia, having a pronounced reflex action, at high concentrations causes a respiratory arrest. There is an anesthetic effect of metallic and tobacco dust on the cornea of the eye.

It was found that the increased fluorine content in the atmospheric air exerts a toxic effect on the development of bone tissue, causing its diffuse compaction. In people living near the aluminum smelter, the hair content of vital elements, such as selenium, chromium, manganese, iron, cobalt, copper, was extremely low. The fluorine content in the hair in some cases was close to the fluorine content in the hair of workers in the production of fluoride [4,10].

In accordance with the most common classification of HCV, according to the main classification of HCV, organs and systems are divided into six groups: general toxic, irritant, sensitizing, carcinogenic, mutagenic, affecting the reproductive (genital) function of the body. General toxic substances (carbon monoxide, lead, mercury, arsenic and its compounds, benzene, nickel, iron (III) compounds, formaldehyde, etc.) cause pathological changes in the whole organism. Irritants (chlorine, ammonia, acetone vapor, nitrogen oxides, ozone and other substances) cause inflammation in the respiratory tract and mucous membranes, with a chronic or acute effect. Iron (III) compounds have cauterizing action on the digestive tract. Chronic intoxication with nickel, iron causes the diseases of nasopharynx, lungs. Sensitizing substances (formaldehyde, various nitro compounds, nicotinamide, hexachlorane, etc.) act as allergens. Carcinogenic substances (chromium (VI), benz(a)pyrene, benzene, formaldehyde, etc.) lead to the emergence and development of malignant neoplasms. Mutagenic substances (manganese, lead, formaldehyde, etc.) cause a change in hereditary information [4].

The lungs adsorb particles of toxic dust easily and ions penetrate into the body's liquid media, and this process is about ten times more effective than the entry of ions through the gastrointestinal tract. Thus, some authors believe that lead, when inhaled, is 10-100 times more toxic than the lead that comes through the stomach [11].

Literary data indicate that in cities with contaminated atmospheric air at a level of 4-8 MPC, incidence of chronic bronchitis increased by 2 times, bronchial asthma by 20%, decreased immunoreactivity in children by 25-30% [12].

Recently, attention has been paid to the study of the possible health consequences of atmospheric pollution with short-term or insignificant fluctuations of pollutants (within 1 MPC). Data are obtained on the dependence of acute effects on the level of individual pollutants (dust, ozone, ammonia, carbon monoxide, sulfur dioxide) [4,12].

Many works of domestic and foreign researchers are devoted to the study of the reproductive function of women living in an unfavorable ecological situation. Direct negative influence of pollutant chemicals on the biological status of the maternal organism and indirect influence of these factors on the fetus was established [13,14].

The literature presents a significant number of studies on the impact of environmental pollution on the children’s health. Because production factors and bad habits do not work for this age group, their health most adequately reflects the influence on the human body of the quality of atmospheric air. It should be noted that in cities with a developed industry in children, as in adults, there is an increase in pathology due to the action of pollutant chemicals, detected in the atmospheric air. The most intensive growth is noted in the following diseases: anemia (2.5 times), chronic diseases of the tonsils and adenoids (4.7), bronchial asthma (4.8), nephritis and nephrotic syndrome (1.7), chronic otitis (1.7 times) [4].

There are data on the quantitative dependence of the incidence of the population on the total air pollution. At the same time, the relative risk of the increase in the incidence of respiratory organs and the cardiovascular system increases by 24 and 12%, respectively, by malignant neoplasms by 5%. It was established that the increase in mortality in settlements with an increased content of pollutant chemicals in the air is observed for the same classes of diseases for which the incidence was recorded [12,15].

According to WHO, the impact of polluted air annually leads to death from 200 to 570 thousand people and this factor accounts for about 0.4 - 1.1% of all deaths per year. The results of epidemiological studies in the US cities showed that in the case of exposure to contaminated atmospheric air, the overall mortality increases by 17-26%, while the rates of infant mortality, mortality from lung cancer, cardiovascular and respiratory diseases increase, life expectancy is reduced by 1 - 2 years [4].

Studies to identify the dynamics of the incidence of the population under the influence of pollutant chemicals emissions and effective measures to protect against the emissions of industrial enterprises require huge material costs, often incommensurable with the revenues of production itself. However, the most significant drawback of the epidemiological method is that it is only applicable to assessing the health effects of existing enterprises.

In many literature sources, it has been suggested to apply methodological approaches to assess the risk of adverse effects of atmospheric pollutants in order to assess the effect of pollutant chemicals on the population health status. It is shown that this methodology makes it possible to identify and assess the quantitative relationships between changes in environmental factors and the characteristics of public health disorders at the pre-pathological and pathological levels.

Analysis of literature data indicates that the methodology of risk assessment is the most adequate methodology for fully taking into account and assessing the impact of environmental factors on public health, and according to experts, this method is widely used in practice.

At present, the ecological situation in the Republic of Belarus has developed as a result of the long-term functioning of the country's economic complex, which operates in the usual technological mode, emergency emissions of pollutants into the environment and their transboundary transfer [16].

The modern ecological state of the country's territory is due, on the one hand, to the degree of economic use, radioactive, chemical and bacteriological contamination of individual components of the natural environment (air basin, soils, surface and groundwater, vegetation) and, on the other, their degree of stability. A comprehensive assessment of the ecological state of the environment of the republic makes it possible to single out the following zones: northern - environmentally favorable, central - environmentally relatively favorable and southern (more precisely southeastern) - environmentally unfavorable and with extremely unfavorable sites (Figure 1).

The map is based on a complex information on pollution of individual components: surface layers of atmospheric air, soil, surface and groundwater, physical factors of influence - noise, vibration and electromagnetic radiation.

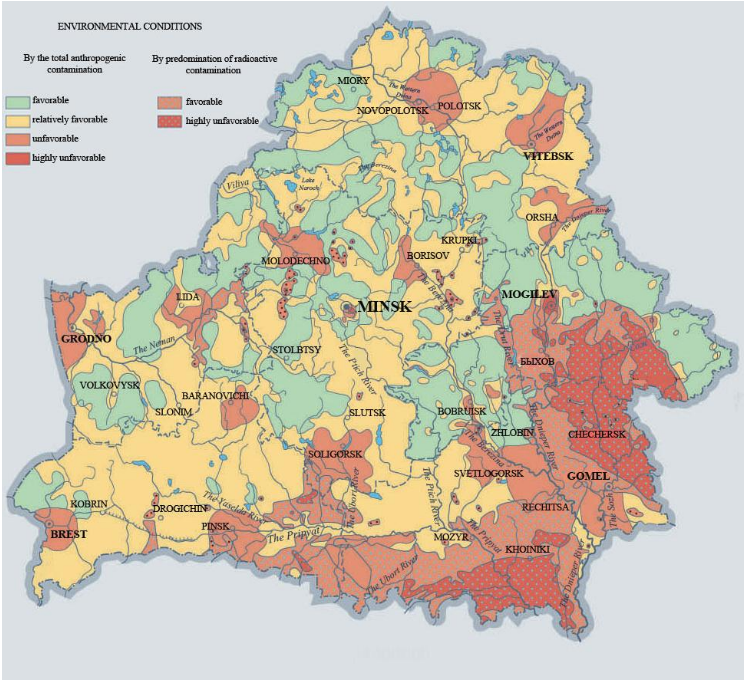

Figure 1 *Ecological condition at the territory of the Republic of Belarus [16]*

The map is based on a complex information on pollution of individual components: surface layers of atmospheric air, soil, surface and groundwater, physical factors of influence - noise, vibration and electromagnetic radiation.

Figure 2 shows a map of the integrated medical geographic regionalization of Belarus, which includes 4 medical-geographical provinces, 45 medical-geographical areas and 186 medical-geographical sub-areas.

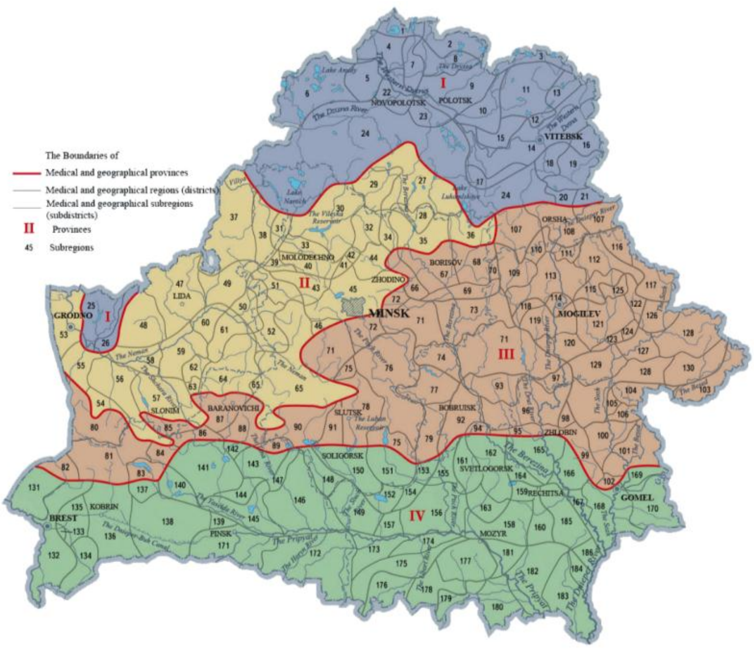

Figure 2 *Integrated medical-geographical zoning of Belarus [16]*

Medico-geographical regions are distinguished according to the incidence and degree of their manifestation. The incidence rate is an absolute value that reflects the distinctive feature of the medical-geographical region. The severity of the incidence is indicated on three levels: low, medium and high. This is a relative value, which indicates the level of manifestation of the disease in this region in comparison with other regions. The severity of the incidence varies with all areas and types of diseases. This indicator is taken as a basis for the allocation of medical-geographical subareas (Table 1).

***Table 1** Indicators of allocation of medical-geographical subareas of Belarus [16]*

The degree of disease severity	General morbidity rates *				
	Thyroid gland diseases	Diseases of malignant neoplasms	Diseases of the endocrine system	Diseases of the digestive system	Diseases of the circulatory system
Low	less 57	less 924	less 3 857	less 9 398	less 11 485
Medium	57-114	924-1 848	3 857-7 714	9 398-18 796	11 485-22 969
High	more than 114	more than 1 848	more than 7 714	more than 18 796	more than 22 969

$$* \frac{\text{number of cases of diseases}}{\text{the number of inhabitants of the region}} * 100\,000 \text{ population.}$$

Maps on the medical and geographical characteristics of the territory of Belarus show not only the existing situation that has arisen with the emergence and spread of human diseases, but also the natural predisposition of the disease.

CONCLUSION

It was found that with the action of small doses of industrial toxicants, the initial reaction of the organism manifests itself in the stimulation of protective mechanisms, which at the first stage does not affect the overall incidence rate. In the future, with prolonged action of man-made pollutants, the incidence may increase abruptly, and with the inclusion of adaptation and resistance mechanisms, the morbidity levels may again return to the previous level, after which the next upswing will occur.

The analysis of literature data indicates that the methodology of risk assessment is the most adequate methodology for fully taking into account and assessing the impact of environmental factors on public health. Experience has shown that this method is widely used in environmental medicine.

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APPLICATION OF RADIOACTIVE ISOTOPES OF COBALT (^{60}Co) AND IONIZING RADIATION PROTECTION IN THE MINING COMPLEX

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Abstract

The work aims to present the application of radioactive isotope of cobalt (^{60}Co) in industrial plant with the maximum protection of professionally exposed workers. On the example of the company it can be seen positive effects of preventive examinations of professionally exposed workers and rehabilitation at the early stage of disease detection. In these considerations it is necessary to take into account the fact that using modern day knowledge we can claim that very small amounts of received doses can cause harmful effects, that is, there is no "threshold dose", below which the received amount doesn't cause, or may cause, no adverse (stochastic or deterministic) effect.

Keywords: Radioactive isotope cobalt, Ionizing radiation, Dosimeters, Occupational diseases

INTRODUCTION

Radioactivity and ionizing radiation were discovered in the late XIX century but is actively exploring after 1945. Its effect on the living world and the ecosystem reminds us of exceptional actuality in modern life (atom bomb, accidents in nuclear power plants, radioactive waste, application of ionizing radiation in medicine, industry) [1].

Problems and risks provoke fear and demand permanent supervision, care and quality professional [2].

Application of ionizing radiation sources in industrial processes is based on interaction of ionizing radiation and material environments.

When passing the radiation beam through the material environment due to the effect of interaction, one part is absorbed, another scattered and the third passes without interaction. Thanks to that, data on the properties of the material environment can be obtained by measuring the amount scattered or missed ionizing radiation [2].

Basic characteristics of cobalt-60 (^{60}Co) radioactive isotope

Cobalt is a hard, gray magnetic material. In nature it can be found as a unique isotope ^{59}Co. It melts at the temperature of 1480°C. Ovening in the flux of thermal neutrons in a nuclear reactor the cores of ^{59}Co capture a single neutron whereby with the emission of gamma radiation pass into the core of an unstable ^{60}Co. Cobalt-60 is the source of photon beam of gamma radiation.

Radioisotopic measurer

Since the system of coal processing is closed with the pressure of 30 bars and under high temperature conditions of 226°C we use radioisotope level gauges because other measurement methods are insufficient and simply impossible.

The measurement technique consists of determining upper and lower levels in the bunker-autoclave, where two measuring devices are placed. Gauge of the upper level is designed for turning off the supply of coal in the bunker when the bunker is filled up to the upper limit, and the gauge of the lower level is designed to give a signal and also, it starts the tapes which are used to fill the bunker with coal when becomes empty, (Figure 1).

In the process of application, radioactive sources ^{60}Co are being stored into special lead-containers which are designed to protect the immediate environment from radiation [3]. In this area, the technique of making ionizing radiation, the technique of production of the appropriate protective container, as well as technique of making sensitive ionizing radiation detectors which allow the use of sources of minor activities, progressed rapidly [4].

The facility "KOLUBARA" has sixteen bunkers with 32 sources of ionizing radiation with built-in ^{60}Co, more precisely: 16 gauges with source of ^{60}Co of initial activity 3.7 GBq and 16 gauges with source of ^{60}Co of initial activity 370 MBq.

Figure 1 *Radioisotopic measurer*

Protection against ionizing radiation includes a range of technical, personal-medical and administrative restrictions whose aim is to reduce the exposure of people to radiation to the smallest acceptable level [5,6].

The basic principles of protection are expressed through the Publications of the International Commission for Radiation Protection (ICRP). Inspector responsible for ionizing radiation sent by Ministry of Science and Environmental Protection Control carries about the implementation of protection measures [7,8].

It is confirmed that even low doses of ionizing radiation can cause harmful effects. Therefore, any unnecessary exposure to ionizing radiation should be avoided and it is necessary to minimize it, the principle ALARA (As Low Reasonably Achievable). Prior to the introduction of ALARA principles, the concept of maximum allowed doses was valid: for professional workers the upper limit was the exposure of 50 mSv per year [9].

Work with ionizing radiation is forbidden for persons under the age of 18, females during pregnancy and after childbirth. Also, persons with prescribed professional qualification and that meet the prescribed health conditions can perform this work [10].

Medical protection measures for persons working with ionizing radiation sources include: medical examination before starting work, overview during work, inspections in the event of an emergency, an accident. With sources of ionizing radiation, people who are ill or have certain diseases can not work [11,12].

In order to control the degree of exposure, i.e. the effective dose received, regular personal dosimeters controls are performed and also, periodic medical examination which are performed once during the year [13].

In the process of coal production thermoluminescent (TLD) dosimeters are used and for each worker a personal dosimeters card is kept in which the values of received doses are entered for a certain period [12].

METHODS OF EXAMINATIONS

Periodic medical examinations of workers of the Mining Basin professionally exposed to ionizing radiation were conducted at the Institute of Occupational Medicine, Department of Preventive Medicine in Belgrade, in the period from May to June 2016, as well as in two subsequent terms (July and November), to give a definitive assessment of the ability of workers.

The analysis examined 211 workers professionally exposed to ionizing radiation. The periodic review program contained all the elements envisaged by the Law jobs with these working conditions and this review: occupational medicine specialist, specialist ORL, ophthalmologist, psychiatrist, lung function testing, hematologic and biochemical analyzes, examination of the urine, biomicroscopic examination of the eye lens.

RESULTS AND DISCUSSION

From a total of 211 workers examined, 14 were female. The average age is 41.95 years. The average total length of service is 19.9 years. The largest number of workers, 116 or 54.98%, said that they occasionally drink, while 90 (43.60%) said they don't not consume alcohol. Only 3 (1.42%) workers stated that they regularly drink. Non-smokers were 97 (45.97%) and smokers 114 (54.03%).

After the examinations were carried out, a total of 398 diseases were found. Grouping of established diseases is shown in Table 1.

***Table 1** Analysis of the morbidity and diseases of the surveyed workers in the period May-June 2016*

Diseases	Number of sick workers	%
Cardiovascular diseases	57	14.32
Respiratory diseases	70	17.58
Gastrointestinal diseases	10	2.51
Endocrine disorders and metabolic disorders	82	20.61
Dermatological diseases	7	1.76
ORL diseases	105	26.38
Neuropsychiatric disorders	16	4.02
Disease of the spinal column and extremities	51	12.81
IN TOTAL	398	100

It is noticeable that the frequency of ORL disorders is common, followed by endocrine disorders and disorders of metabolism (obesity, hyperlipidemia, hypercholesterolemia, hyperglycemic disease), and respiratory diseases (most commonly, deviations of the nasal septum and chronic rhinitis).

It should be noted that in the group of neuropsychiatric disorders it stands out anxiety disorders (5 workers). One worker was diagnosed with mental disorders and behavioral disorders caused by the use of opiates, and at one worker a behavioral disorder caused by the use of alcohol has been identified.

Out of 211 surveyed workers who are professionally exposed to the ionizing radiation source, 40 of them (18.95%) have a limited capability to work (Figure 2).

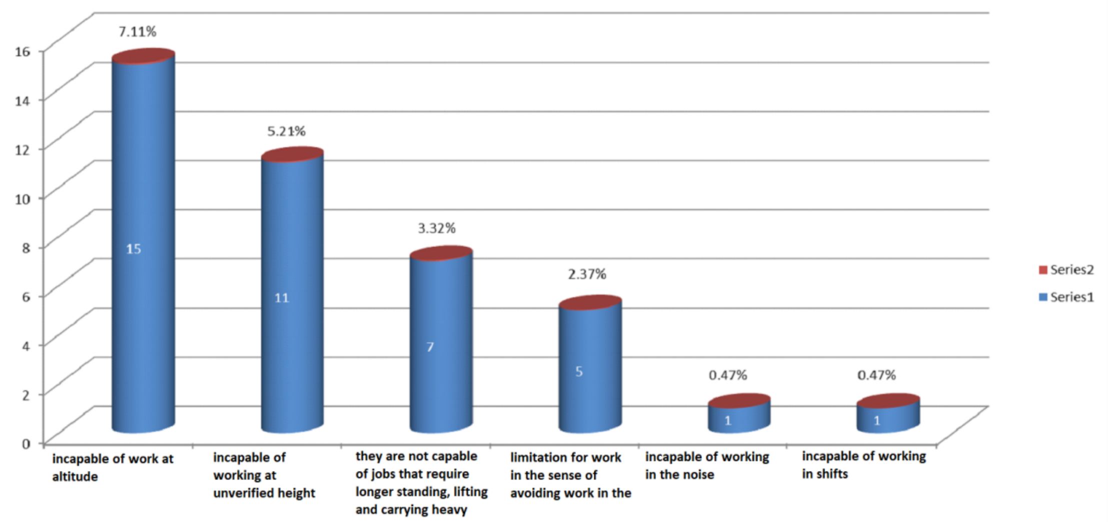

***Figure 2** Assessment of working ability*

Proposal measure

The present state of use of devices for detection of ionizing radiation in the industrial coal processing in the Mining Basin should not be the aim, but only the starting point for further work and improvement. Radiation Dosimetry is a scientific field which research and find applications of radiation. People who are working on Occupational Safety work are obliged to follow modern achievements of Radiation Dosimetry and apply them. The aim is to protect professionally exposed persons as efficiently as possible [14].

Personal dosimetric protection via TLD dosimeters is not sufficiently protective measure from ionizing radiation in the workplace of professionally exposed people. It is also necessary to use protective clothing, aprons, rubber gloves, glasses.

Regular health examination of 211 workers revealed that ORL diseases and endocrine disorders are the most often. It is necessary to remove diseased persons from the workplace and allocate them to a easier job in order to prevent further deterioration of the health.

In the Occupational Safety Service, it is necessary to employ an environmental sanitary engineer who would with his knowledge and expertise complete the team that is currently working on these jobs.

CONCLUSION

Application of sources of ionizing radiation in the coal processing is considered justified because it gives a positive net benefit. A system of protective measures that includes technical measures and legislative standards of protection “Exposure to ionizing radiation” is 10 (ten) times lower than the recommendation of the International Commission for the Protection of Ionizing Radiation for Professionally Exposed Persons. Protection against the harmful effects of ionizing radiation is within the limits of an equivalent and effective dose-via TLD dosimeters.

The user of the ionizing radiation source provides prescribed and regular checking of the fulfillment of health conditions of persons working with sources of ionizing radiation and provides periodic renewal of knowledge of persons working with sources of ionizing radiation.

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SOFTWARE DEVELOPMENT FOR THERMOVISION APPLICATION IN TRIAGE PROCEDURES OF EMERGENCY CONDITIONS

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Abstract

Thermovision as a diagnostic method is increasingly being used in various spheres in the world. This trend also implied the application of thermovision in medicine as a new diagnostic method. The possibilities of using thermovision in medicine are increasing every day. Accordingly, the development of a dedicated software solution, which is used in medical diagnostics using thermovision, is shown in the paper. The presented software solution is developed using the open-source solutions, with almost no realization costs. Also, the developed software works on open source solutions, so the costs of implementing and maintaining the software solution itself are minimized, too. This is a significant increase in the possibility of one wider accepting thermovision recording as a new diagnostic method in medicine.

Keywords: Diagnostic procedures, Linux, Thermovision, Thermal imaging, Software

INTRODUCTION

In recent years, there has been an increase in the use of thermovision principles and solutions in various spheres, whether it's scientific, research, or some industrial application. Such a trend has the consequence that thermovision solutions are constantly moving through various cycles of innovation and improvement and are becoming more modern and more acceptable. Thermovision on the market of diagnostic solutions today takes an increasing share, making thermovision solutions more applicable in a wider spectre of use. Such solutions are becoming less complex in various aspects of use, simpler to implement, operate, maintain in preventive, operative and post-operative meaning, leading to an increasing economic feasibility of introducing such solutions.

Some of the most commonly used thermovision applications and solutions based on the use of thermovision in industry and manufacturing are in the field of electricity distribution and control of power plants, control and monitoring of the operation of electronic equipment, in various types of metallurgical plants, for controlling the operation of production plants, in the process industry, in oil and gas industry, heat treatment, water supply, civil engineering. There are also some special cases of thermovision solutions such as the application of thermovision in ecology, the protection of borders and objects, fire control from the ground and from the air, in aviation, as well as in various areas related to research and development [1].

In recent years, the importance of using thermovision in various branches of medicine has grown, for example, in the field of sports medicine [2]. Intensive researches are conducted for analysing the possibilities of using thermovision in cancer detection in early stages. In general, one of the major, possible, applications of thermovision in medicine is in diagnostic procedures. Thermovision methods can be one of the cornerstones of future trends in the development of diagnostic methods in modern medicine because of their potential efficiency and ease of implementation and application.

This paper is based on one such potential application of thermovision in medical diagnosis purposes and in the following considerations will be analysing and presented one software approach related to that potential application.

THERMOVISION IN MEDICAL DIAGNOSIS

Non-invasive methods in medicine for the diagnosis of the patient condition, have always had one of primary importance [3]. Modern medicine implies today the use of more familiar methods, their variations and mutual combinations in modern diagnostics. The basics of many of these methods have been known for decades, but their adequate application gets a new meaning by using ideas and modern approaches that introduce new technical and technological discoveries in diagnostics. Most commonly used diagnostic methods worldwide today are Radiography (X-rays) [4], Computer Tomography (CT Scan, CAT Scan) [5], Magnetic Resonance Imaging (MRI) and Nuclear Magnetic Resonance (NMR) [6] and Bone Scan [7].

As previously said, there are efforts to include thermovision and its techniques in accepted diagnostic methods in medicine as modern non-invasive method.

Thermovision as a term means recording the intensity of radiation in the infrared portion of the electromagnetic spectrum and translating obtained data into an understandable, visible image [8]. Special equipment (usually this special equipment is so called thermovision camera) can detect infrared radiation and on the basis of it form a temperature picture of the observed object. This method is called thermovision or infrared thermography [1]. On the corresponding obtained image, each pixel that builds the resulting image essentially shows one of the temperature characteristics of the object itself. This is enabled by complex algorithms built into the software of thermovision cameras that allow conversion and formation of pixel image-temperature relation of the corresponding detected infrared radiation of the part of the object [9]. The image generated by the action of thermal radiation is called a Thermogram (also known as Infra-Red Image or Temperature Map) [1].

These basic thermovision principles are also used when the thermovision is used as a medical diagnosis method. According to Stolić *et al*. [10] thermovision camera is equipment for medical analysis of the patient using “the point and shoot” principle. That means that the camera is pointed to the part which is diagnosed and then the infra-red image of that part is recorded (“shoot”). Image contains all necessary temperatures which will be further analysed in aim to provide enough information about the patient state. By direct observation of the thermovision image, appropriate temperature zones can be detected which can lead to the identification of the hotspot in the recorded part. For detailed assessment of patient condition special software is used for calculations of temperature differences and their comparison with corresponding scale. That scale based on mentioned temperature differences indicates appropriate levels of alerts: normal, monitoring, prevention, high alert and very serious condition [2].

Based on provided insights which can be very precious and fast estimated using thermovision procedures, patients can be further diagnosed and the treatment can be started in very short time. One of the key future of thermovision diagnosis is that it can be obtained very fast over the patient without the need for the patient to be dislocated to another facility or department. First response with thermovision can be realized at the desired place in very short time and with very small use of resources.

THERMOVISION SOFTWARE

There are various types of software on the market which can be used for work with thermovision images. Most of vendors shipped appropriate software with thermovision equipment, but the common practice is that shipped software has some basic functionalities and for some additional functions some other version of software must be purchased separately [11]. This increasing costs of implementing thermovision solutions because in most case there are need for adaptation of software for the particular case.

Some of the mentioned common basic functionalities provided by the thermovision software are:

1. **transferring images from a thermovision camera to a computer for the purpose of storing or further processing,**
2. **application of appropriate tools over thermovision images,**
3. **grouping of thermovision images,**
4. **creation of reports related to specific thermovision recording,**
5. **upgrading the thermovision camera software (upgrading the firmware).**

Those functionalities provides capabilities which can be used for manipulation with recorded thermovision images, but in some cases that functionalities are not enough for further processing and in some cases that functionalities are limited.

In case represented in Stolić *et al*. [10], using of this kind of software is unproductive for some reasons. First in that particular case software must be easy and not confusing without redundant options. Also, for this particular case software only need to give insights to detected hotspots during recording of the patient.

THERMOVISION SOFTWARE APPROACH FOR USE IN TRIAGE

According to previously, authors are developed special software for case described in Stolić *et al*. [10]. The abstraction through block diagram of the developed software is shown in Figure 1.

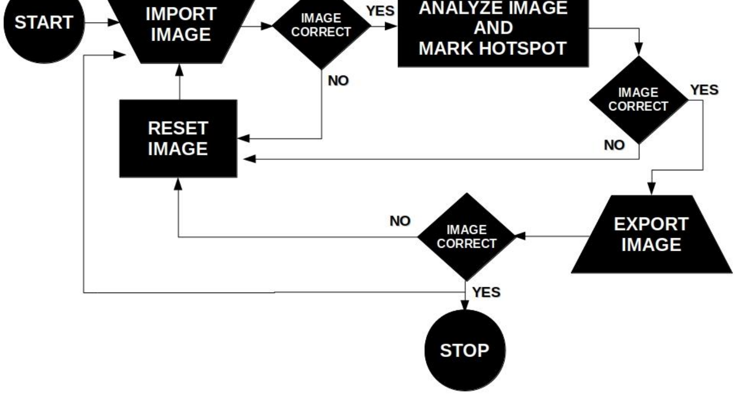

Figure 1 *Block diagram of developed software*

Software imports a thermovision image, analyzes it and detects the hotspot. At the end, the thermovision image with a marked hotspot is recorded as a separate image that can be used in further diagnostic work. At any time, if the problem with imported thermovision image is noticed, imported image can be reset and returned to the initial state in the form of the original thermovision image.

In accordance with the presented block diagram, the basic options of the realized software are identified. The following options for working with the mentioned software are noted as it shown in Figure 2:

- **Importing of a thermovision image (Учитавање термовизијског снимка),**
- **Reseting a thermovision image (Ресетовање термовизијског снимка),**
- **Analysis of thermovision image (Анализа термовизијског снимка),**
- **Saving the results of the analysis (Снимање резултата анализе) and**
- **Exit from the program (Излазак из програма).**

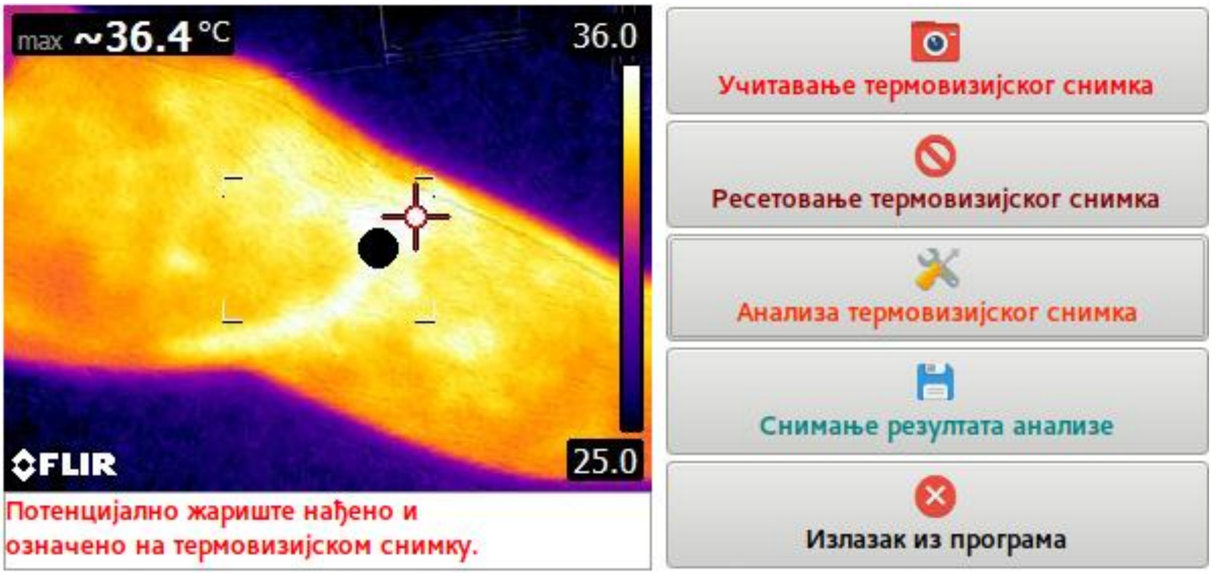

Figure 2 *Snapshot of the software during the work with thermovision sample and after the identification of the hotspot on thermovision image*

The software consists of three parts. In the first unit (the rectangle with the thermovision image on the left side), all thermovision images used in the software are displayed (original thermovision image and thermovision image with pointed hotspot). The other part of the software that occupies the right side of the display, which is used within the software, has options available to the user of the software. As already mentioned, these options are fully consistent with the integral parts shown in the block diagram. The third part which is located in the lower left corner (white framed rectangle) is the part where the status messages of the software itself are displayed in order to give a better insight into the actions executed while working with the software and performed the operation over the desired thermovision image.

The whole development of the software is done in the Linux environment, so the software is basically intended for work under various Linux distributions and their graphic systems. But, using the cross compiling method, the mentioned software could be quickly and efficiently made to work within different Windows environments, as well as work in Mac OS and other environments. The software was successfully tested on several well-known Linux distributions: Fedora Core, Canonical Ubuntu, OpenSUSE. In all of these distributions, the software passed all tests with stable operation in all fields of its functionality. The thermovision images for work within the software are given in a 320x240 JPEG format, since the software is specifically designed for use with the FLIR Thermovision Camera E5 Series. Software can be easy adapted for use with other thermovision cameras, but at the moment of development authors have only mentioned camera, so other cameras are not implemented and tested. For the development, Lazarus Integrated Development Environment (Lazarus IDE) 1.6 was used under the Linux Fedora Core 24 operating system, based on the use of FPC (Free Pascal Compiler) version 3.0. Lazarus is an Open Source development platform. In order to allow full compatibility with various systems and in order to enable later cross compiling of the source code, the LCLIntf library was used during development. In development, GTK + 2 was also used under the Gnome graphical interface to create a user graphical interface and all accompanying graphic elements. To manipulate with thermovision images, standard library sets for manipulation with images of different formats were used, but they were using only a limited set of functions and procedures intended exclusively to manipulate the JPEG image format.

During the analysis, all the pixels in the specified range are read. Reading the pixels is done by reading the values according to the RGB model used to generate a thermovision image, or the values for red, green and blue (RGB - Red, Green and Blue). The values obtained in accordance with good practice and universal access are converted to hexadecimal values that are synthesized in a unique code that determines each pixel by color. At the same time, information on the position of pixels per x and y axis on the thermovision image is stored. After obtaining these values, a comparison of the pixel of a given thermovision image can be made to find the pixel with the maximum value that represents the centre of hotspot on the thermovision image recording.

An individual pixel is very difficult to spot on the image because in this particular case it is necessary to identify one pixel in relation to 57000 pixels from thermovision image. Accordingly, a suitable hotspot instead of a single pixel is presented with some more suitable shape. It was decided that the hotspot should be presented with a circle of black color and with the radius of 20 pixels that is very visible on the thermovision image. The black color represents the substantially minimum values of red, green and blue (zero values) and is taken as a highly contrasting color, since the colors of the thermovision image are extremely bright. The radius of the circle is obtained as the ten-percent value of the image width. This approach enables a clear identification of the hotspot on a thermovision image as shown on Figure 2.

CONCLUSION

The camera manufacturers usually provide, for the development of special thermovision solutions, theirs SDK (Software Development Kit), but in most cases it is not publicly available. Mostly, it is a commercial product, so there are some limitations for using in the development of the dedicated software. Accordingly, in the paper independent software solution is developed from scratch used various open source solutions. Using this kind of development, realized software is publicly available without any commercial limitations.

Using the Linux operating system and its ecosystem during the overall software development and in the final software implementation, software realization costs are almost equal to zero. These facts improve the ability for installation of thermovision solutions in various medical facilities included ones with a very small budgets which usually cannot afford expensive diagnostic solutions. By this way it is possible to implement, on the one side, very mobile and cheap and on the other side, effective and futuristic diagnostic solution.

Extensive research in scope of using thermo vision recording in medicine is still ongoing and breakthroughs in this domain are expected in the near and far future. It can be said with certainty that the importance of thermovision and thermovision recording in medicine will grow and that we can expect that at one moment “thermovision diagnostic” will be included in standard diagnostic medical methods around the world. Realization of the software mentioned in the paper is one of the factors which increase chances for standard thermovision diagnostic in medicine in the near future and the prediction is that whole software packages like presented one will be increasingly available on the global market.

ACKNOWLEDGEMENT

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ANALYTICAL METHODS USED TO EVALUATE WHOLE MILK QUALITY

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Abstract

Milk is an emulsion of fat globules and protein micelles in an aqueous phase containing lactose, minerals, and other minor constituents. Milk composition measurement can be completed by wet chemistry or instrumental methods. Chemistry methods are more time consuming and polluting. The experiments had in view to study the correlation between some physical properties (relative density, viscosity and surface tension) and the main chemical parameters, in order to use the best analytical methods in milk quality appreciation. The milk physical properties are influenced by the dispersion degree of the components, so that proteins have a greater influence on these parameters. The obtained experimental data revealed that the protein content is highly positive correlated with the relative density (r = 0.7582) and the dynamic viscosity (r = 0.7953), and negative correlated with the surface tension (r = -0.8052). Milk fat has a smaller influence on the physical parameters, being negative correlated with relative density (r = -0.5855) and surface tension (r = -0.5643), and positive correlated with dynamic viscosity (r = 0.5637).

Keywords: Milk, Relative density, Dynamic viscosity, Surface tension, Protein, Fat

INTRODUCTION

Milk is an emulsion of fat globules and protein micelles in an aqueous phase containing lactose, minerals, and other minor constituents. Milk, at the time of secretion, comprises an aqueous phase (including lactose, whey proteins, minerals, and water-soluble vitamins) and a lipid phase (including fat globules, fat-soluble vitamins, and other hydrophobic components). The main milk organic components are the proteins (casein, lactoalbumin, and lactoglobulin), lactose, and fat [1-5]. Casein is the main protein in cow's milk. It can be fractioned by electrophoresis into four major components: alpha-, beta-, gamma-, and kappa-casein. Caseins are phosphoproteins, with molecular weight >20,000 which are precipitated at pH 4.6 (for cow's milk) or by action of the enzyme chymosin (rennin). Other whey proteins present in smaller amounts are serum albumin, immunoglobulins (e.g. IgA, IgG, IgM), protease, peptones, lactoferrin, and transferrin. Casein forms with albumin colloidal dispersions. Lactose, the main ingredient in whey, is a reducing disaccharide composed of D-galactose and D-glucose [2]. Lactose (β-D-galactopyranosyl-(1→4)-D-glucose) content of milk varies between 3.6 and 5.5%. Lactic acid bacteria, containing the enzyme lactase, split lactose molecule into glucose and galactose. Glucose and galactose are converted by other enzymes from the lactic-acid bacteria into mainly lactic acid [6]. Milk fats consist of a mixture of compounds including triacylglycerols, diacylglycerols, monoacylglycerols, phospholipids, cerebrosides, gangliosides, sterols and sterol esters and derivatives, carotenoids, tocopherol, vitamins A, D, E, C, B1, and B2, and free fatty acids [7]. Fat in milk is present as fat globules ranging from 0.1 to 15 μm in diameter. Milk fat globules are the largest particles in milk and also the lightest. These globules are covered by a thin membrane that helps to stabilize the emulsion within the aqueous environment of the milk [8-10].

Chemistry methods are more time consuming and polluting. These analyses are considered primary methods of milk component determination. Instrumental methods are rapid, non-polluting, and have very low cost per test. The operator training and skill required is significantly lower for instrumental testing [11,12].

The experiments had in view to study the correlation between some physical properties (density, viscosity and surface tension) and the main chemical parameters, in order to choose the best instrumental methods in milk quality appreciation.

MATERIALS AND METHODS

The experiment was made on raw milk samples collected from 20 dairy cows. Milk samples were cooled to 8°C immediately after milking and transported to the laboratory. Standard laboratory methods were used to analyze the milk samples [13]. The principal components in milk were determined with an infrared spectrophotometer LactoScope Analyzer (Delta Instruments) [14]. Gravimetric determination of milk density was conducted using an analytical balance (Kern ABJ 220-4M) with given uncertainty ±0.0001 g and a standard volumetric pycnometer (25 mL) [15,16]. The pycnometer was previously calibrated with distilled water for each temperature kept constant using a thermostatic water bath (LabTech LSB-015S). The dynamic viscosity was determined using a cone/plate viscometer (Brookfield Model DVIII Cone CP-40) at 60 rpm. The surface tension was measured using the dynamic stalagmometric method (drop number method) [17].

For each parameter, the samples were analyzed in three replications. Results were expressed as mean ±*SD* of three separate determinations. The statistical significance of the differences among the mean values was tested by ANOVA.

RESULTS AND DISCUSSION

The chemical and physical parameters of the milk samples were within the normal limits (Table 1).

Table 1 *Biochemical and biophysical parameters of milk samples*

Fat (g %)	3.135± 0.582
Protein (g %)	3.177± 0.337
Casein (g/L)	24.28±2.494
Total Solids (g %)	12.053± 0.777
Relative density	1.032 ± 0.00074
Dynamic viscosity (cP)	1.5381 ± 1.1105
Surface tension (Nm^{-1})	48.5755± 4.2099

Milk density is the summary result of the densities of its various components. It is dependent on the amount of dissolved or suspended matter, changes in chemical composition of the constituents, and variations in physical states of components. The mean value of milk relative density was 1.032±0.00074 (ranging from 1.030 to 1.034). Shortly after the milking, density is low, primarily due to the change of the aggregate state of the fat particles, which are contracted upon cooling (solidifying). The density of milk should not be determined for at least one hour after it is drawn from the animals, otherwise a lower-than-normal value will be obtained (due to the Recknagel phenomenon). A high fat content decreases the relative density of milk, while a high protein, lactose and mineral salt content increases the specific weight. Since fat has a lower specific gravity and therefore is "lighter" than the milk serum (relative density at 15°C is about 0.9307), fat globules rise to the milk surface. The obtained experimental data revealed a negative correlation between relative density and fat content (r = -0.5855) (Figure 1).

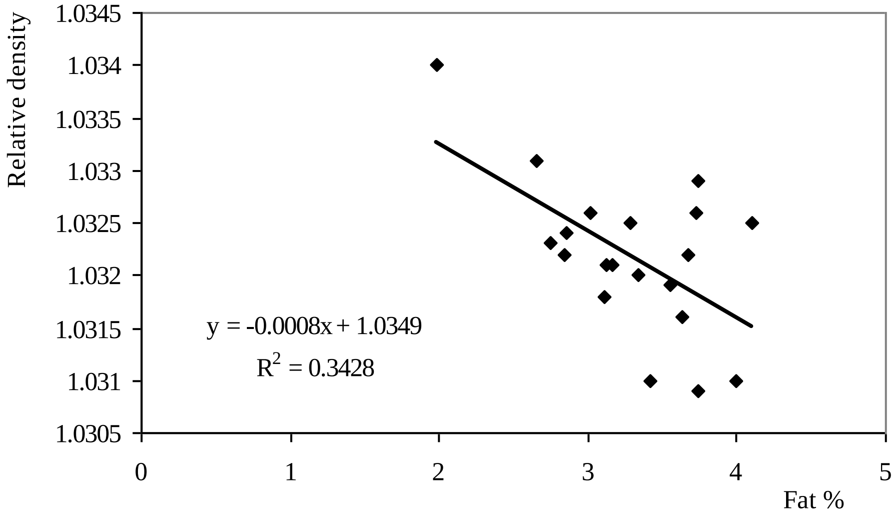

Figure 1 *The correlation between relative density and fat content*

The relative density of the degreased dry matter, i.e. protein, lactose and salts at 15°C, is 1.601. The obtained experimental data revealed a high positive correlation between relative density and protein content (r = 0.7582, P<0.001) due to casein micelles with the dimensions of 10-100 nm and density of 1.11 g/mL (Figure 2).

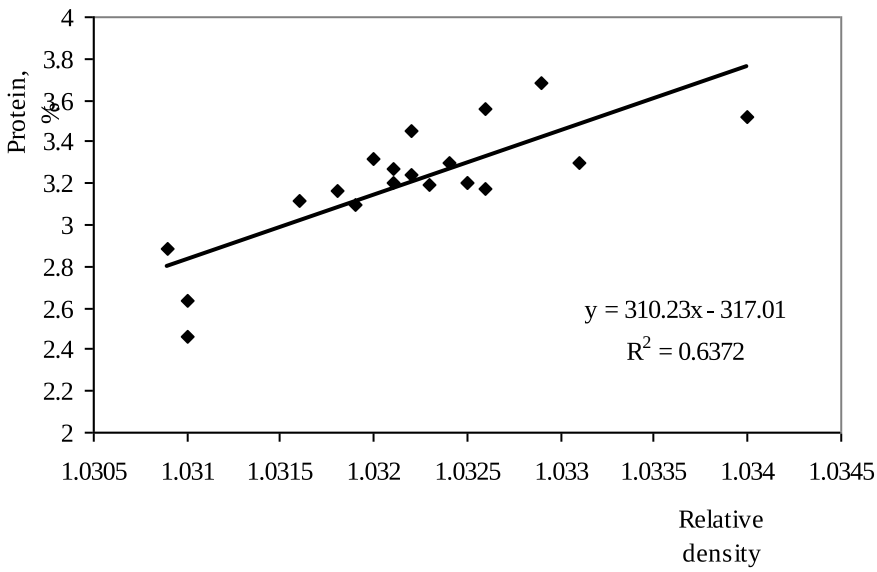

Figure 2 *The correlation between relative density and protein content*

The surface tension of whole milk is 0.7–0.8 of that of water, proteins being surfactants. A negative correlation between superficial tension and protein content of milk (r = -0.8052) was observed (Figure 3). Milk proteins influence mostly the surface tension and the dynamic viscosity. The milk physical properties are influenced by the dispersion degree of the components. Casein (diameter 0.1-0.005μ) and albumin (diameter 0.015-0.005μ) form colloid dispersions. Most of the casein proteins exist in colloidal form, known as the casein micelle. Colloidal calcium phosphate acts as cement between hundreds or even thousands of submicelles that form the casein micelle. Binding might be covalent or electrostatic. Although casein is a lyophobic protein, its effect is to lower the surface tension [5].

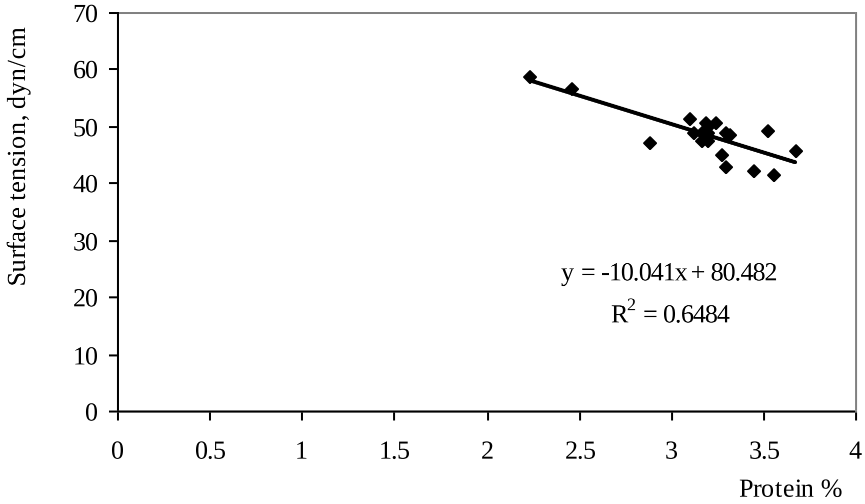

Figure 3 *The correlation between surface tension and protein content*

Surface tension decreases with increasing fat content The interfacial tension between milk fat globules and the milk serum is about 2 Nm^{-1}, while the interfacial tension between non-globular, liquid milk fat and milk serum is about 15 Nm^{-1}, indicating the effectiveness of fat milk globule membrane material in reducing interfacial tension [18,19]. There is a negative correlation between surface tension and fat content (r = -0.5643) (Figure 4).

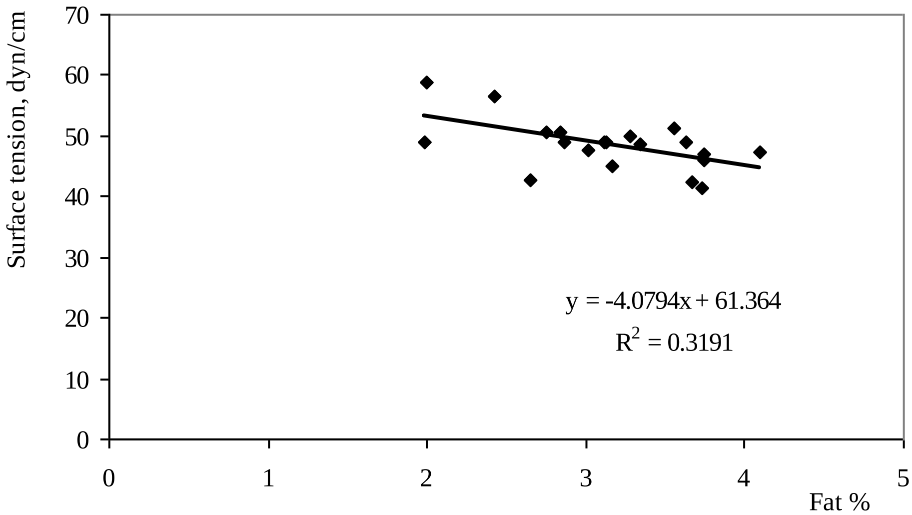

Figure 4 *The correlation between surface tension and fat content*

Measurements of viscosity have been recognized necessary to provide fundamental insights on rheological property of milk. Milk and skim milk, excepting cooled raw milk, exhibit Newtonian behaviour in which the viscosity is independent of the rate of shear. The change in milk viscosity was depended on the contents of milk fat and milk protein. The dynamic viscosity of the analyzed samples ranged between 1.30338-1.73685 cP. A high positive correlation was observed between the dynamic viscosity and the protein content (r = 0.7951) (Figure 5). The degree of protein dispersion has a major effect on viscosity. The viscosity of colloidal systems depends upon the volume occupied by the colloidal particles. Casein is the component that contributes mostly to the viscosity change. It forms colloidal dispersions together with albumin, which acts as a casein stabilizer by its protective colloid effect.

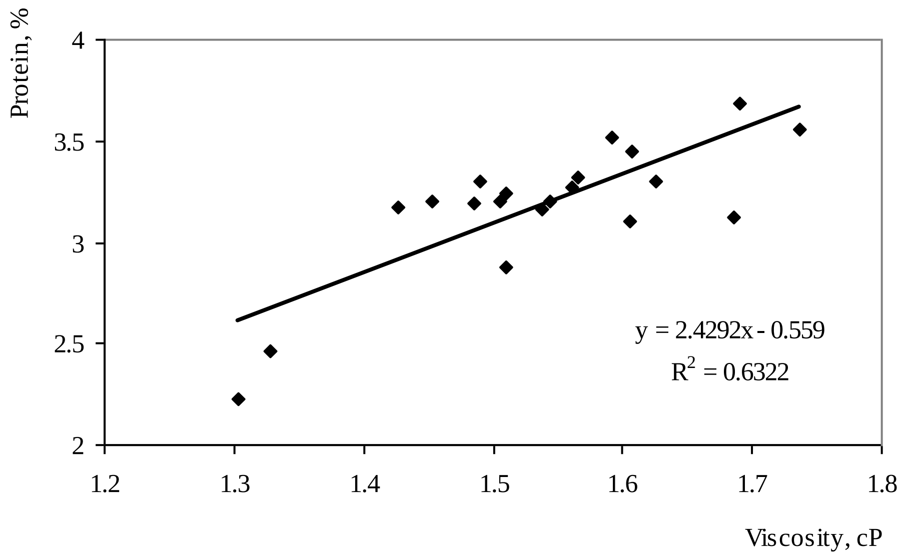

Figure 5 *The correlation between dynamic viscosity and protein content*

A positive correlation was observed between dynamic viscosity and concentration of fat (r = 0.5637) (Figure 6).

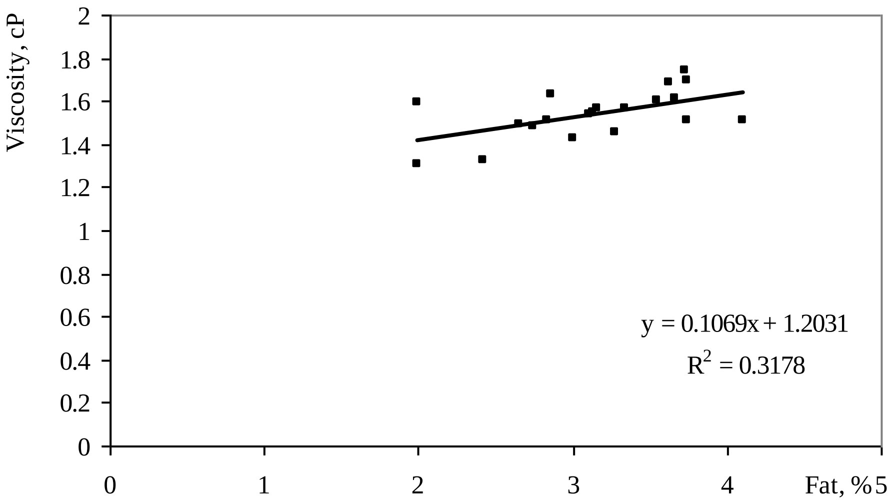

Figure 6 *The correlation between dynamic viscosity and fat content*

CONCLUSION

The milk physical properties are influenced by the dispersion degree of the components, so that proteins have a greater influence on these parameters. The obtained experimental data revealed that the protein content is highly positive correlated with the relative density (r = 0.7582), and the dynamic viscosity (r = 0.7951), and negative correlated with the surface tension (r = -0.8052). Milk fat has a smaller influence on the physical parameters, being negative correlated with relative density (r = -0.5855) and surface tension (r = -0.5643) and positive correlated with dynamic viscosity (r = 0.5637).

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EVALUATION OF THE FUNCTIONAL PROPERTIES OF SOME BREAKFAST CEREALS

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Abstract

Dietary fiber (DF) includes non-starch polysaccharides resistant to digestion in the small intestine and fermentable in the large intestine: arabinoxylan, inulin, pectin, bran, cellulose, β-glucan and resistant starch. Consuming adequate quantities of DF has beneficial physiological effects: improving gastrointestinal health, decreasing cholesterolemia and glycemia, and preventing heart disease and cancer. The physiological parameters of DF are influenced by their physicochemical properties, especially by the soluble DF fraction, as this is responsible for the changes in intestinal viscosity. Increased intestinal viscosity delays the nutrient absorption, the passage rate and increases the bile acid excretion. Food processing, such as flaking, has great effects on DF, especially on the molecular weight distributions. The experiments showed that on flaking, the water retention capacities were higher compared to unprocessed cereal samples. Aqueous extracts of cereal flakes had much higher relative viscosity (RV) than the raw cereals, caused by the structural and physicochemical changes. Although total fiber values of the flakes are comparable to those of raw cereals, a redistribution of insoluble to soluble fiber occurred. While increasing the solubility of β-glucans and arabinoxylans, the most important water-extractable polysaccharides, an increase in RV of aqueous extracts was also observed.

Keywords: Water retention capacity, Viscosity, Flaking, Dietary fiber, Cereals

INTRODUCTION

Dietary fiber (DF) is the primary determining factor for the quality of products constituting the base of the nutrition pyramid. DF includes non-starch polysaccharides resistant to digestion in the small intestine and fermentable in the large intestine: arabinoxylan, inulin, pectin, bran, cellulose, β-glucan, and resistant starch [1]. Based on their water solubility, DF may be grouped into two forms: insoluble dietary fiber (IDF) such as cellulose, part of hemicelluloses, lignin, and soluble dietary fiber (SDF) such as pentosans, pectins, gums, some hemicelluloses, and mucilages [2]. The conversion of IDF into SDF by chemical treatment, affects the sensory properties of the products. Grains and cereal foods, fruits, vegetables, legumes, nuts, and seeds are important sources of DF [3]. Fruits and vegetables contribute less towards fiber, having higher water content. Grains are considered to be the richest sources of DF. The amount of DF coming from cereal products differs to a great extent depending on the source and the processing of the item [4].

DF has an important role in improving of the human health. Consuming adequate quantities of DF has beneficial physiological effects: improving the gastrointestinal health, decreasing the cholesterolemia and glycemia, and preventing the heart disease and cancer, by improving the metabolism of lipids and sugars [5-8]. Low energy value of whole-grain products permits also the maintenance of correct body mass index and thus prevents epidemic occurrence of overweight and obesity [9,10]. The beneficial effects of DF, especially SDF, on diseases associated with the Western lifestyle are primarily attributed to their ability to modify the viscosity of the intestinal content. The physiological parameters of DF are influenced by their physicochemical properties, especially by the SDF fraction, as this is responsible of the changes in intestinal viscosity. The ability of fibers to form viscous solutions is determined by the concentration, solubility, the polymer molar mass and aggregate formation. The viscous property of SDF refers to the ability of the fibers to thicken solutions when mixed with fluids. IDF can also increase viscosity, but only to a minor extent. An increase in viscosity along the gastrointestinal tract may result in increasing the bile acid excretion, delayed gastric emptying, trapping of macronutrients, bile acids, estrogen or digestive enzymes in the viscous network, and/or slower mixing and diffusion. SDF performs important physiological functions and also acts as a prebiotic, improving host health, being a substrate food for beneficial microorganisms [11].

Several properties determine the viscosity of solutions of DF: solubility, molar mass, aggregation, and water-holding capacity. Fibers that have charged groups interact more favorably with polar solvents, such as water, which increases their solubility. Changes in pH affect the charge and polarity, leading to lower solubility and the formation of networks and gels. Side-chains and structural irregularities also lead to less network formation and hence, a higher solubility [12,13]. Milling to a smaller particle size promotes solubility due to the increase in surface area and by opening physical barriers, allowing fluid penetration [14].

A high molar mass contributes to increased viscosity, but at the same time to decreased solubility. The molar mass differs between fiber sources, and can be influenced by processing techniques [15]. The ability of polymers to associate, forming macromolecular aggregates can increase the viscosity [16]. Small molar masses increase the degree of aggregation due to higher diffusion rate [17]. A high water-holding capacity can also increase viscosity [18]. Mechanical treatment can cause shearing damage, influencing the particle size, the fiber structure and interactions, as well as depolymerisation [19]. High temperatures can also influence the structure causing depolymerisation of fiber chains, and may lead to a reduction in the viscosity. On the other hand, smaller fiber particles and/or a smaller molar mass will increase the solubility, which is also necessary for increased viscosity. Insufficient heating can result in unsuccessful deactivation of endogenous enzymes, which in turn can depolymerise the fibers. Frozen storage has been reported to decrease the solubility of β-glucans in oat products [20]. Repeated freeze-thaw cycles have also been demonstrated to cause physical changes and gelation (forming of cryogels) in several polymers, which have been suggested to decrease the viscosity [21]. The ability of some forms of DF to form gels has been suggested to delay or inhibit nutrient uptake in the small intestine, although the relationship between gelling and physiological effects is not yet fully understood [22].

The aim of the present study was to investigate the effect of flaking on two functional properties of some breakfast cereals: the water retention capacity (WRC), and the relative viscosity of aqueous extracts (AERV).

MATERIALS AND METHODS

Some cereals: wheat (W), barley (B), corn (C) and commercial cereal flakes: 3 types of wheat flakes (WF1, WF2, WF3), 3 types of barley flakes (BF1, BF2, BF3), oat flakes (OF) and corn flakes (CF) were analyzed for WRC and AERV. The samples were milled by a laboratory grinder to pass through a 500 μm sieve. WRC was determined using the method of Anguita *et al*. [23,24], and expressed as grams of water retained by 1 g dry matter (DM). The water-soluble fiber fraction was isolated by a single 1:2 extraction for 60 minutes at 40°C. Dynamic viscosity of aqueous extract was measured at 25°C using a Wells Brookfield Cone/Plate Digital Viscometer Model DVIII Cone CP-40. All results were expressed in cP and calculated also as values relative to that of water (AERV).

RESULTS AND DISCUSSION

Food processing, such as flaking, has great effect on DF, especially on the molecular weight distribution. Experimental values of WRC in extruded cereal samples (Figure 1) were higher compared to unprocessed cereal samples. The highest value was obtained for corn flakes (3.05 g/gDM).

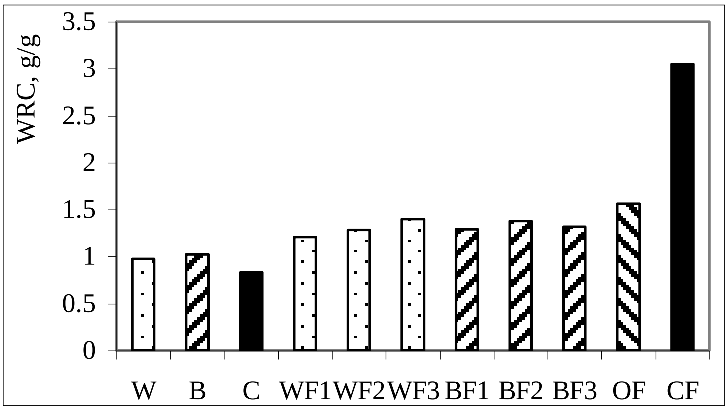

Figure 1 *WRC of grains and cereal flakes*

Cereal flakes had much higher values for AERV than raw cereals, caused by the structural and physicochemical changes. During processing occurs also formation of new fiber components, e.g. resistant starch or products of the Maillard reaction [25]. The increase in the level of DF in cereal flakes is related to increasing content of resistant starch, due to the process temperature. Although the total fiber values of the flakes are comparable to those of raw cereals, a redistribution of insoluble to soluble fiber occurred. Flaking resulted in an increased degradation of the molecular mass of DF. This caused a reduction in the content of insoluble DF fraction and an increase in that of the soluble fiber fraction. Consequently, the determined extract viscosity is increased. Experimental data showed that processed cereals have much higher AERV than the unprocessed grains (Figure 2).

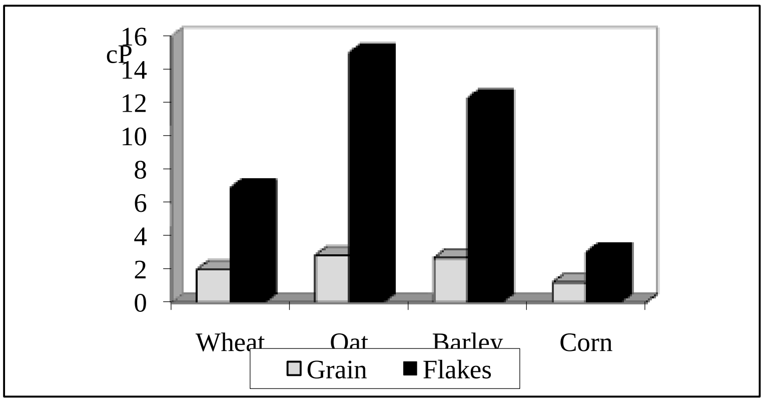

Figure 2 *AERV of grains and cereal flakes*

While increasing the solubility of β-glucans and arabinoxylans, the most important water-extractable polysaccharides [26,27], extrusion produced an increase in AERV. Extrusion increased mostly the AERV of wheat, barley and oat (3.48 times in wheat, 4.56 times in barley, and 5.26 times in oat). Corn meal fiber was less affected by extrusion under the same conditions as the other foods. The viscosity measurement of aqueous extracts prior to ingestion can be used to predict the intestinal viscosity of processed cereals.

Data obtained show that AERV varies with fiber content (Figure 3). A high positive correlation (r = 0.9079) between AERV and DF content of processed cereals was observed (Figure 4). AERV of processed cereals was negatively correlated (r = -0.6487) with the total carbohydrates content (Figure 5).

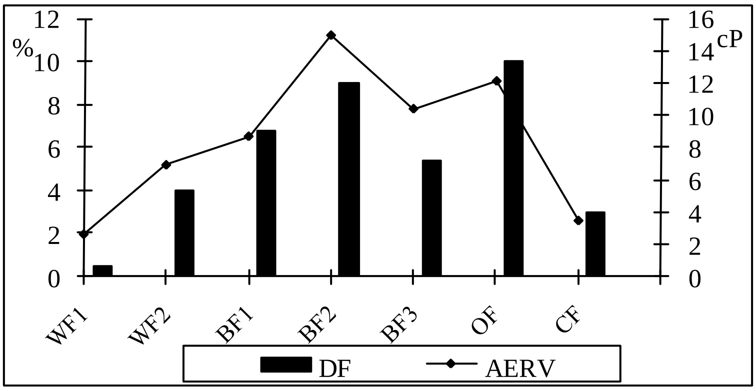

***Figure 3** AERV and DF content of cereal flakes*

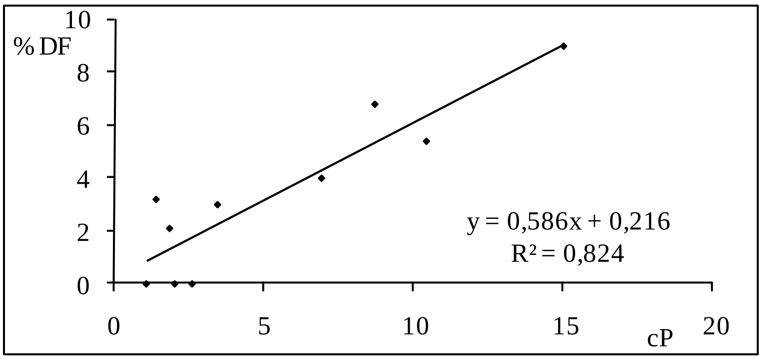

***Figure 4** Correlation between AERV and DF content of cereal flakes*

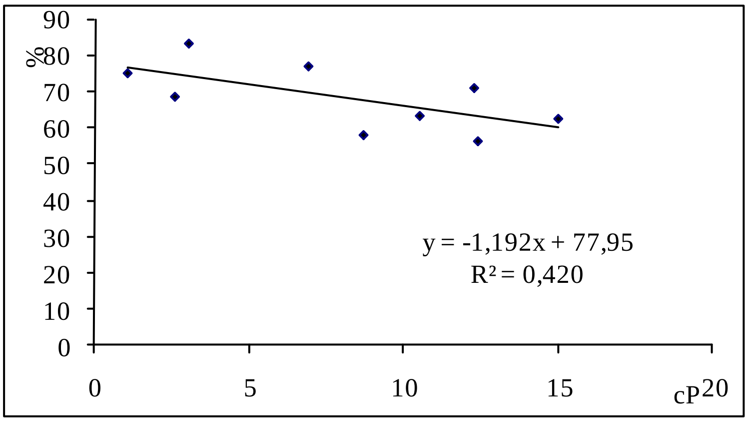

***Figure 5** Correlation between AERV and carbohydrate content of cereal flakes*

CONCLUSION

Water retention capacity of studied cereals is increased by flaking, the highest value was measured in corn flakes. Extrusion increased mostly the viscosity of aqueous extracts of wheat, barley and oat (3.48, 4.56, and 5.26 times, respectively); corn was less affected. The relative viscosity of aqueous extracts is high positively correlated (r = 0.9079) with the dietary fiber content of processed cereals, and negatively correlated (r = -0.6487) with the total carbohydrates content.

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BIOLOGICAL ACTIVITY OF ESSENTIAL OILS ON THE *Tribolium confusum* (Coleoptera, Tenebrionidae) ADULTS

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Abstract

Tribolium confusum Du Val (Coleoptera, Tenebrionidae) is one of the most widespread pests in mills in our country and warehouses all over the world. Conventional control of harmful insects in the warehouse implies the use of insecticides. Continuous use of pesticides led to reduced efficacy and resistance. That is why there was a need for finding alternative ways of protection. According to this, the toxic effect of essential oils of mint (Mentha piperita), basil (Ocimum basilicum) and hyssop (Hyssopus officinalis) was examined. The tested concentrations for all three plants were: 25, 50 and 100 µl/ml. The experiment was set in four replicates for each plant, concentration and control. Twenty adult insects were placed in containers and the mortality by examined essential oils was observed after 24, 48 and 72 hours. After 24 hours the strongest toxic effect caused the essential oil of mint by the highest concentration of 100 µl/ml with a mortality rate of 67.5%. The same concentration caused a mortality rate of 72.25% after 48 h and 73.75% after 72 hours which is the highest mortality rate achieved in this study. Essential oil of hyssop and basil led to mortality rate between 1.25 and 10% after 72 hours.

Keywords: *Tribolium confusum*, Essential oils, Biological activity, Insecticidal effect

INTRODUCTION

Harmful insects, who live exclusively in the warehouses on food leftovers, which man prepares for their own needs, originate from nature. They lived thousands of years ago in the nature and ate various plants, seeds ect. The beginning of collecting and storing food reserves by the people is probably the beginning of adaptation of some insect species to the new conditions of life [1].

Losses in grains due to infestation during storage are a serious problem, particularly in developing countries. Damage to stored grains and their products range from 5 to 10% in the moderate climate, while in tropical areas are 20 to 30% [2].

Botanical insecticides, repellents and inhibitors of nutrition represent an alternative to the classical method of protection by insecticides [3]. The need for it arose for several reasons. Continuous use of pesticides has led to reduced efficacy of insecticidal effects, resistance, persistence, toxic effects on non-target organisms and concern for human health and the environment [3-6].

There are a number of plants which could be used to control harmful organisms because of their biological activity [5]. Some plant extracts are toxic to the target, some are repellent and others work as attractants [7]. Certain secondary metabolites of plants have an important role in the interaction of plant-insect and they are responsible for the resistance of plants to insects.

The use of botanical insecticides in stock is promising, mainly due to the possible control of environmental conditions within the warehouse, as well as maximizing the insecticidal effect. Botanical insecticides can be used as a powder, extract and oil [4].

MATERIALS AND METHODS

For the purposes of experimentation, the adult insects of *T. confusum* were used, grown in the laboratory of Entomology at the substrate, in a thermostat at the temperature of 27 ºC and relative humidity of 50%. Essential oils of mint, basil and hyssop were extracted by the process of hydro-distillation on the Institute of Field and Vegetable Crops. Experiment was set up, for each of the three essential oils, in glass containers of cylindrical shape (diameter of 7 cm and a height of 3.7cm) with a protective cap. The experiment was set up in four replications for each concentration and control; 20 adult insects were placed in each container.

Essential oils of mint, basil and hyssop were applied in the amount of 50 µl per filter paper. Tested concentrations for all three plants were: 25, 50 and 100 µl/ml, while for the control was used an equal volume of n-hexane. Filter papers with applied concentrations were placed in the plastic plugs which were covered with perforated parafilm. Parafilm was used as prevention from direct contact between insects and essential oils. The plugs and 20 insects were placed in glass containers and then containers were closed and wrapped with a parafilm. Number of dead insects was counted after 24, 48 and 72 hours.

Statistical analysis of data was performed by the basic statistic methods and tests, and it was also observed correlation connection of *T. confusum* mortality, depending on the plant species from which is extracted essential oil, the concentration of the essential oil, as well as the time of reading, using the software STATISTICA 13 (StatSoft, University License).

RESULTS AND DISCUSSION

Effect of the inhalation activity of essential oils of mint, basil and hyssop was tasted by a number of dead insects *T. confusum* after 24, 48 and 72 hours. Mortality rate (%) of *T. confusum*, which was caused by applied essential oils, is shown in Tables 1, 2 and 3.

Table 1 *The effect of essential oil of mint (Mentha piperita) on the T. confusum*

After 24h	Replicates				
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	9	16	6	17	60
50	13	9	13	14	61.25
100	16	9	13	16	67.5
Control	0	0	0	1	1.25
After 48h	Replicates				
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	10	16	6	17	61.25
50	15	15	13	14	71.25
100	19	9	13	17	72.25
Control	0	0	0	1	1.25
After 72h	Replicates				
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	11	16	7	17	63.75
50	15	16	13	14	72.25
100	20	9	13	17	73.75
Control	0	0	0	1	1.25

After exposure of insects for a period of 24h essential oil of mint at the concentration of 100 µl/ml showed the highest insecticidal effect (67.5%), while at lower concentrations, depending on the concentration, the insecticidal effect was from 60 to 61.25%. After 48 h mortality rate was 72.25% at the highest concentration of 100 µl/ml. After 72 hours, the mortality of insects at the highest concentration 100 µl/ml was 73.75%, while mortality rate at the other concentrations was within the range from 63.75 to 72.25% (Table 1).

Table 2 *The effect of essential oil of basil (Oscimum basilicum) on the T. confusum*

After 24h		Replicates			
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	0	0	0	0	0
50	0	0	0	0	0
100	0	0	0	0	0
Control	0	0	0	1	1.25
After 48h		Replicates			
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	0	0	0	0	0
50	0	0	0	0	0
100	0	2	0	0	2.5
Control	0	0	0	1	1.25
After 72h		Replicates			
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	0	0	0	0	0
50	0	0	0	0	0
100	1	2	0	0	3.75
Control	0	0	0	1	1.25

After 24h exposure, the insecticidal effect was not manifested, while after 48 hours, the insecticidal effect showed the highest concentration of 100 µl/ml with a mortality rate of 2.5%. Insect mortality after 72 hours was 3.75% in the case of the highest concentration of 100 µl/ml (Table 2).

Table 3 *The effect of essential oil of hyssop (Hyssopus officinalis) on the T. confusum*

After 24h		Replicates			
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	0	0	0	0	0
50	0	1	0	0	1.25
100	0	0	0	3	3.75
Control	0	0	0	1	1.25
After 48h		Replicates			
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	1	0	0	0	1.25
50	0	1	0	0	1.25
100	0	0	0	4	5
Control	0	0	0	1	1.25
After 72h		Replicates			
Concentration (µl/ml)	I	II	III	IV	Mortality rate (%)
25	1	0	0	0	1.25
50	0	1	0	0	1.25
100	1	2	1	4	10
Control	0	0	0	1	1.25

After exposure in a period of 24 hours essential oil of hyssop at a concentration of 100 µl/ml showed the highest insecticidal effect (3.75%) on *T. confusum* and at the concentration of 50 µl/ml the insecticidal effect was of 1.25 %. After 48 h, mortality was between 1.25 and 5%, whereas after 72 hours the mortality of insects at the highest concentration (100 µl/ml), was 10% (Table 3).

Statistical data processing

In order to determine the statistical significance of the percentage mortality of *T. confusum* as the dependent variable and the plant species from which is extracted essential oil, the concentration of the essential oils and the time of reading as independent variables, multifactorial and factorial analysis of variance (ANOVA) was applied using Statistica 13 software package (StatSoft, University license).

Existence of statistical significance was determined in the case of the essential oil as the independent variable on the mortality rate as the dependent variable (pb=0.000000 for $p < 0.05$) (Figure 1). Fisher's LSD test showed the existence of statistical significance between mortality rate of mint essential oil and the mortality observed in the application of basil and hyssop, as well as the mortality in the control (Table 4).

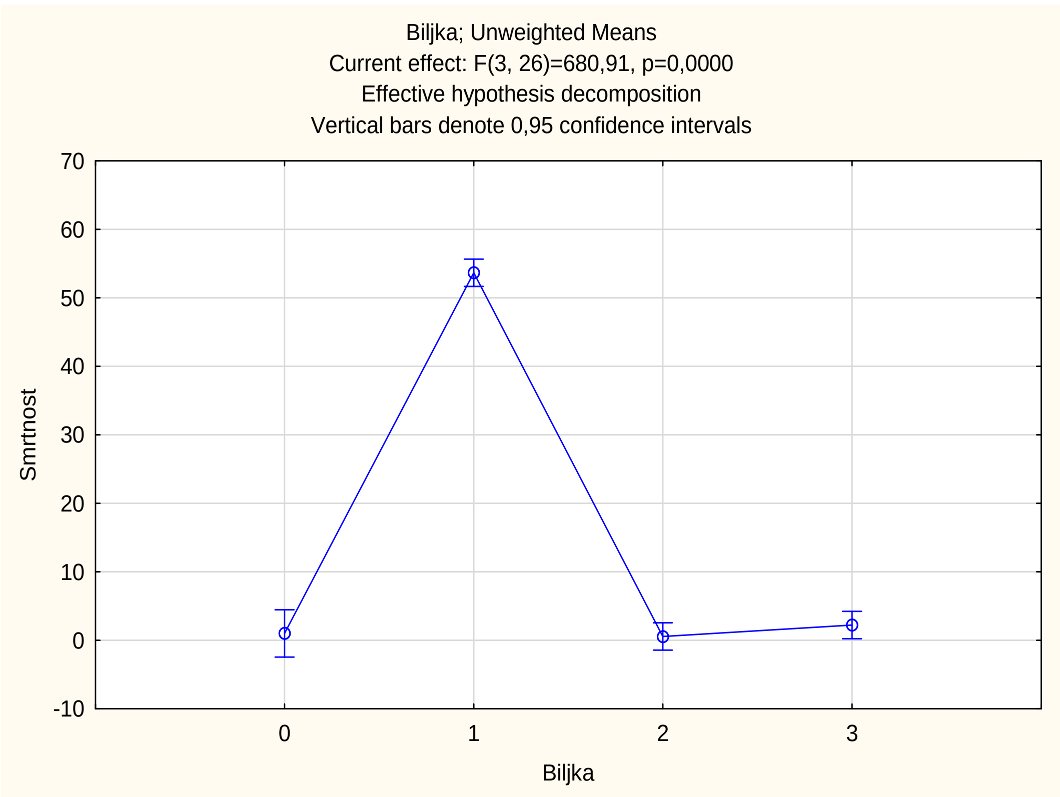

Figure 1 *The operation of the plant species as the independent variable on the mortality as dependent variable*

Table 4 *Fisher's LSD test for the operation of a plant species as the independent variable on the mortality as dependent variable*

LSD test; variable Mortality (Spreadsheet1) Homogenous Groups, alpha=0.05.
Error: Between MS=8.4530, df=26.00

Plant species	Mortality Mean	1	2
Basil	0.55556	****	
Control	1.00000	****	
Hyssop	2.22222	****	
Mint	53.66667		****

CONCLUSION

After 24 hours, the strongest toxic effect and the highest percentage of the dead insects caused the essential oil of mint by the highest concentration of 100 µl/ml, with a mortality rate of 67.5%. The same concentration caused a mortality rate of 72.25% after 48 h, which was 73.75% after 72 hours and that is the highest mortality rate achieved in this study. Essential oil of hyssop and basil showed poor insecticidal activity and mortality was between 1.25 and 10%, after 72 hours.

Furthermore, statistical significance was determined between plant species, which were used for extraction of essential oils, as independent variables on the mortality as dependent variable. Fisher's LSD test showed the existence of statistical significance between mortality rate of mint essential oil and the mortality observed in the application of basil and hyssop, as well as the mortality in the control.

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MANAGING SUSTAINABLE TOURISM AND HOTEL INDUSTRY IN MACEDONIA: ENERGY RESOURCES STRATEGIC APPROACH

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Abstract

The study is focused on presenting some insights into the use of energy in the hotel industry in Macedonia. It aims at providing an assessment of managerial perception of energy resources and discussed more environmentally compatible and sustainable alternatives. The data were collected by means of an online survey conducted among hotel managers and department supervisors. The summarized results point that the problem is a substantial gap that exists between managerial awareness for the benefits of the renewable energy, and the daily practice of hotels. The study recommends that hotels should create specific strategies that will have a significant impact on reducing energy consumption. Some aspect of these strategies may include increasing the level of awareness among hoteliers through a direct and well-designed environmental protection campaign. Furthermore, to develop and introduce a wide range of energy efficient practices in the first line by introducing some renewable sources of energy. Finally, the paper argues that extraordinary luxury and sustainability are not mutually exclusive by presenting some sustainability best practices of worldwide applied standout environmental programs.

Keywords: Sustainability, Hotel management, Strategic development, Energy, Tourism

INTRODUCTION

The hotel sector is energy-intensive and makes tourism a substantial contributor to negative impacts on the environment. This requires new technologies that will enable hotels to use cleaner and cheaper energy sources, thus assisting in reducing operational costs and increasing competitiveness and sustainability. Yet, adopting sustainable policies is no longer a simple trend, but it becomes a necessary reality. So, wasting less food, saving energy, acting in a less harmful way towards the environment, adding value to the brand, and pleasing customers, is a positive practice for everyone.

Generally, tourism accounts for about 5% of greenhouse gasses (GHG) emissions worldwide, out of which the largest proportion of 75% is associated with transportation, whereas 40% is caused by air traffic [1]. Another factor that contributes to the environmental footprint of tourism is accommodation. This sector represents approximately 20% of GHG emissions generated from tourism [2]. The variety of tourism types, which rely on clean nature and unpolluted environment as core values, impose the necessity to strive for sustainable tourism. Consequently, hotel management introduces such energy practices that enable environmental protection by reducing carbon dioxide, methane, nitrous oxide and other harmful emissions that provoke global-warming and climate changes. Yet, despite the gain in efficiency, the emissions from global tourism sector are predicted to grow 161% by

2035 [2]. This actually means that tourism implicates many negative effects that must be prevented or at least, decreased.

Around 90% of the primary energy in Macedonia is produced from fossil fuels, mainly lignite and heavy crude oil, so the energy sector contributes with over 70% in total emission of GHG resulting with enormous pollution. Based upon the State of Environment report [3], total emissions by sectors in Macedonia are due to combustion processes (60%), transport (30-40%), and other (less than 5%), along with 12% of recycled packaging.

Within the Strategy for Energy Development in Macedonia, it is foreseen to increase competitiveness in the wider regional energy market and to become high energy efficient [4]. It is proclaimed by 2020to achieve improvement of energy efficiency by 20%, provision of energy from renewable energy sources (RES) in the amount of 20% of the final energy consumption, and at least a 10% share of RES in the final energy consumption in traffic [5]. So, maximizing the RES utilization is among strategic priorities, which is proved by the constant increase from 4.2% (2012) to 13.8% (2005) [6], making Macedonia a country with a relatively high RES utilization [5]. Moreover, based on many scenarios within national strategic documents, it is indicated that Macedonia can set the RES target share at 21% [7].

An option is to source own energy by applying renewable energy as a realistic alternative. Hotels particularly become aware and commit themselves to significantly reduce the energy used by them and eagerly look for cheaper energy sources that will contribute to sustainable and ecologically sound future. Although this paper contributes to the current research on energy savings in tourism and hotel industry in Macedonia [8-12], its main contribution lies in the intention to provide insights into the processes how Macedonian hospitality industry stakeholders manage environmental quality. It has a practical significance since it discusses the level of environmental quality of Macedonia, while simultaneously posing facts how some of the most energy-efficient luxury hotels in the world apply green initiatives. In times when energy prices have been high for a number of decades, it is more than justified to introduce incentives for hotel properties to go down the alternative energy route.

The paper is structured in several parts. After the introductory part, the following section presents the methodology and research findings on the applied environmental policy in Macedonian hotels. This is followed by a section that presents few cases as best green practices from hotels around the world. The article's final section offers the main conclusion and poses some recommendation on the investigated issue.

METHODOLOGICAL NOTES, FINDINGS AND DISCUSSION

In order to enlighten the process how Macedonian hotels manage environmental quality, an online research was conducted in June 2016 among managers of three, four and five-star hotels. The main goal was to assess the perception of hotel management in the application of sustainable programs. Besides general data, the online questionnaire comprised of two hardcore set of questions addressing the issues of Environmental Policy, and Resources usage. Out of 127 identified managers, only 45 responded, representing a response rate of 35.4% standing as a relatively high for an online survey.

The Environmental policy part of the questionnaire consisted of eight yes/no questions related to the application of sustainable policies, practices, and programs. It was found that five-star hotels have by far the most positive environmental concerns since they claim to hold a Certificate for energy efficiency along with the four-star hotels, unlike the lower ranked hotels in Macedonia. The same is the finding for written plans for environmental protection, whereas surprisingly half of the three-star hotels claim to prepare it. Yet, none hotel type prepares reports on environmental protection which is not in favor of supporting the European environmental impact assessment regulation. In this line, vast majority of three and four-star hotels do not have Eco label (80.0% of the three-star hotels, and 52.6% of the four-star hotels), do not hold Eco certificate (80.0 % of the three-star hotels and 73.7% of the four-star hotels), and do not have personnel responsible for environmental protection (68.8% of the three-star hotels and 52.6% of the four-star hotels). On the other hand, the findings completely differ in the case of five-star hotels, whereas half surveyed managers stated to have Eco label (50.0%) and Eco certificate (60.0%). Although in favor (70% claimed to have it), there is a certain risk in the interpretation and understanding the question related to the term 'personnel for environmental protection' which might be understood as a 'personnel in charge for cleaning the environment', which in most cases is a job of the housekeeping staff. Furthermore, none of the surveyed three and four-star hotels have ever received an award related to the environmental protection, although they have been working for over 15 years, strongly supports the general finding concerning environmental policy in Macedonia that still needs to be done. However, the positive impulse is detected in providing info to guests related to environmental protection, which points to the rather social responsibility of hotels and lack of energy efficiency practices.

The third part of the questionnaire consisted of eleven questions addressing the issue of applying different types of resources in hotels work. By categorizing responses in a 5-point Likert scale, the managerial perception of energy use and resource conservation was evaluated. General findings are alarming since they point to the extremely limited use of alternative sources of energy and new innovative approaches to saving energy consumption. The research found that the mean values for the extremely important RES are very low pointing to the lowest power when quantifying the item's impact. So, mean values for the items referring geothermal energy, biofuel, photocell lighting, as well as the use of treated water, are far below the critical indicating that these determinants are meaningless for the hotels' energy efficiency concept. The dimming system, which in general increases the lifespan of incandescent and LED light sources, is a smart, silent, reliable and efficient system for saving energy in hotels. Yet, this item is perceived as only a low impact determinant used extremely limited by Macedonian hotels.

On the other hand, solar energy and the "smart rooms" operations, are perceived as medium usage, while the use of energy saving systems that control every appliance in rooms and key-card control system that provides no power unless the room-key is inserted, along with the energy saving light bulbs, are found as resources with strong impacts. Very similarly, the central cooling/heating system along with the guest demands for linen and towel changes are assessed as very strong factors of influence on hotels business. The guests' awareness of energy efficiency is constantly rising by having the choice to use the same towels and linens for the duration of the stay, rather than to incur the environmental costs of laundering them each day. This conservative measure is practiced by each hotel regardless the categorization and simultaneously increases the guest satisfaction and loyalty by showing their care for energy efficiency and climate change.

GREEN HOTEL PRACTICES

A hotel may provide fully luxurious guest experience and be very green at the same time, in a manner that is practical, economic, and aesthetic. Figure 1 presents that extraordinary luxury and sustainability are not mutually exclusive. Moreover, it presents some sustainability best practices of worldwide applied standout environmental programs.

The main driving force why these facilities decided to become sustainable hotels is their commitment to leave as small an environmental footprint as possible. Moreover, the key objective of their sustainability programs is to ensure to be truly sustainable in all aspects of development principles being incorporated throughout the hotels' operations and in interactions with stakeholders and communities. Hence, their commitment to sustainability is deep and genuine. In this line, such green and sustainable hotels encompass a range of projects, like: recycling up to 94% of the waste; installing energy efficient equipment; reducing water consumption with efficient shower heads; installation of solar panels to generate green energy on-site; green procurement of recycled and biodegradable materials; involvement in community greening initiatives; etc. Almost all hotels carried out major modifications and redevelopment changes to the resorts including upgrades to air-conditioning by including new cooling towers, variable speed drives, as well as building management system and energy monitoring throughout the resorts by sub-metering all electrical metering points.

a) Hotel Bordessano, Yountville, California, USA [13]

b)Vineyard Hotel & Spa, Cape Town, South Africa [14]

c) Novotel Jaragua, Sao Paolo, Brasil [15]

d) Fairmont Resort Blue Mointains, Leura, Australia [16]

***Figure 1** Photovoltaic solar systems in hotels worldwide*

Hotel Bordessano in Yountville, California, USA is one of few hotels in the U.S. that was certified LEED Platinum certification in 2015, due to its readiness to ensure environmental sustainability. The hotel installed a roof-top solar array (Figure 1a) that contributed to approximately 50% of total electricity consumption, with 6-8 years expected payback period based on electricity costs and subsidies. The primary motivation was reducing the reliance on petroleum and other fossil fuels, thus making this hotel one of the greenest in the world.

By applying many energy savings projects, hotels significantly may reduce operating costs, where lighting, HVAC (heating, ventilation and air conditioning) and water-heating approximately accounts for 60% of total costs. So, The Vineyard Hotel & Spa in Cape Town, South Africa (Figure 1b) installed new laundry system and saved 34% energy compared to the old system, along with LED lights installed in the conference center which resulted in 75% energy saving.

Besides automation system that controls and reduces the use of each machine, saves energy and money, as well as installation of energy control in every guest room, and installation of heat exchangers that transforms the heat in the ambiance with boilers into energy to heat the water for guests' rooms, Novotel Jaragua in Sao Paolo, Brasil (Figure 1c) developed own vegetable garden that produces organic and free pesticide products. The solar-powered plants are producing clean energy and the harvested food is used by its own restaurants, guaranteeing the quality of each product.

The Fairmont Resort Blue Mountains in Leura, Australia installed a 100 kW PV solar system, out of which 30 kW is on the Golf club house's rooftop (Figure 1d). By this, the hotel has savings of 885 kWh/week through a reduction in energy, gas, and water throughout the resort. Furthermore, the installed PV solar system provides CO_2 savings in the range of 155.7 kg/per year for the Fairmont Resort and saves additional 46.3 kg/per year only for the Golf clubhouse. The use of solar energy is part of an integrated environmental energy management strategy, which also includes a 'smart' system allowing lights and air conditioning to be turned off in rooms when the guest is away and for ambient room temperature to be varied according to the outside temperature. This hotel also added a variable speed drive system on all air conditioning pumps, which allows better management of flows according to demand from guest rooms and common areas.

CONCLUSION

Hotels must strive to make their facility to fit as an integral part of the local environment, but not to impede it. They must apply such policies that are based on strict environmental requirements. If the hotel operates in a sensitive natural environment, it should adopt and make a strong point of optimum sustainability practices. It is not sufficient just to talk about environmental good intentions, but the hotel has to embrace and promote sustainability.

Although energy projects led to savings, massive investments need to be done into infrastructure, whereas the consumption effect is immediate, but it takes several years until the capital investment is offset. On the other hand, the hotel maximizes its use of renewable energy only if ensuring efficient operations by installing high-efficiency ground-source heat pump system for heating and cooling needs, high-efficiency lighting, expansive windows for natural daylighting, guest room occupancy sensors that control lighting and conditioning, and automatic blinds to minimize unnecessary heat again.

The study recommends that hotels need to go one step further and take sustainability seriously enough to employ a specialist to manage energy efficiency, water conservation, waste reduction and community social responsibility. Additionally, it was found that one of the most important impacts of the sustainability programs and the biggest challenge in implementing environmental policy is the human factor. There is a need for increased awareness and change in behavior among staff as well as guests, who must be educated and motivated to implement hotel's sustainability policy. It may be concluded that building and managing eco-friendly hotel is a big accomplishment, and the effort requests strong motivation by hotel managers and supervisors.

The research concludes that Macedonian hotel managers need to be truly aware that being ecologically responsible is paramount. The research survey found that many managers do not buy into the initiatives, or do not understand why they are important. Hence, it is impossible to achieve profound change. This has to be embedded in the core business of the hotel facility and cannot be treated as a secondary matter. Becoming eco and sustainable hotel means involving all stakeholders (employees, suppliers, customers, society, etc.). Only when managers show that small changes can produce incredible results, then hotels may expect to gain more results. Many positive examples of green and sustainable hotels prove that guests specifically choose to stay at such hotel because of its environmentally-friendly operations and minimized footprints.

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TYPES OF SMART GLASSES AND THEIR USE IN ARCHITECTONIC DESIGN OF ENERGY EFFICIENT BUILDINGS

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Abstract

In recent years, the market for light - control glass has expanded due to the increasing demands for energy efficiency and heat and light control, automated shading, privacy, and design and engineering innovation. Smart glass is a unique type of glass that is able to change its light transmission properties, based on external stimuli. It is typically classed into active and passive smart glass. Passive smart glass changes its properties according to the presence of external stimuli such as heat and light. Based on the stimulus, it can be categorized into the following types: Thermochromic (TC) and Photochromic (PC) smart glass. Active smart glass requires an electrical stimulus to change its properties. Based on the type of technology used, active smart glass can be categorized into the following types: Electrochromic (EC), Liquid Crystal (PDLC) and Suspended Particle Device (SPD). Currently, the Architecture sector accounts for 11.01 percent of the market - the second largest application area for smart glass globally. The adoption of larger window sizes and glazing areas in European countries will also boost the demand for smart glass during the forecast period. The paper analyzed the types of smart glasses, their advantages and constructed buildings where smart glasses were used.

Keywords: Glasses, Smart, Types, Architecture, Energy

INTRODUCTION

The objective of meeting the growing demand of thermo-hygrometric and environmental comfort, associated with an urgent need to improve the energy efficiency of buildings to achieve "carbon neutral" or "zero energy buildings" (ZEB), is necessitating a thorough review of the building envelope characteristics and requirements, directing toward technological solutions that can provide a continuous adjustment of the set of environmental flows in relation to climatic conditions (Table 1).

In fact, the building envelope plays a crucial role in the energy performance of a building, significantly affecting the comfort levels of the indoor environment [1]. Over the last fifty years glass technologies for buildings have undergone radical changes and extended the functions and applications of glazing in modern architecture. The industry is slowly but surely turning its attention toward more advanced glazing materials and the emerging technologies described as “smart glass" [2,3]. These smart materials are able to respond to seasonal variations in temperature and solar radiation. Such advancements in ‘smart’ windows will stimulate the continued use of glass as a building facade and also reduce the energy

Loads associated with achieving a comfortable internal environment (Figure 1) [3]. In addition, glass is made of abundant non-polluting raw materials, its manufacturing process is highly energy efficient, requires low levels of water and generates little waste. In fact, recent life-cycle studies have shown that windows represent a very minor share of a building's environmental impact from the concept to the construction phase.

Table 1 *Interrelation in building design [4]*

Interrelation in building design					
Environmental system		Building system		Human system	
Cultural context	Physical context	Building technology	Internal ambience	User requirements	Client objectives
social	Climate	Available resources	Structural mass	Organic	Security
Economic	topographical	Material equipment	Sensory environment	Locational (static/dynamic)	Profit
Technological	Constrains	Structural systems	(lighting/ sound control/ heating/ vent	Spatial	The ability to change
historical		Services system			
political					
aesthetic		Fitting system			
religious					

Nowadays, a vast array of glass and glazing solutions exists to satisfy the needs of the most ambitious architects and building engineers who want to design and construct low energy or passive buildings [2,3].

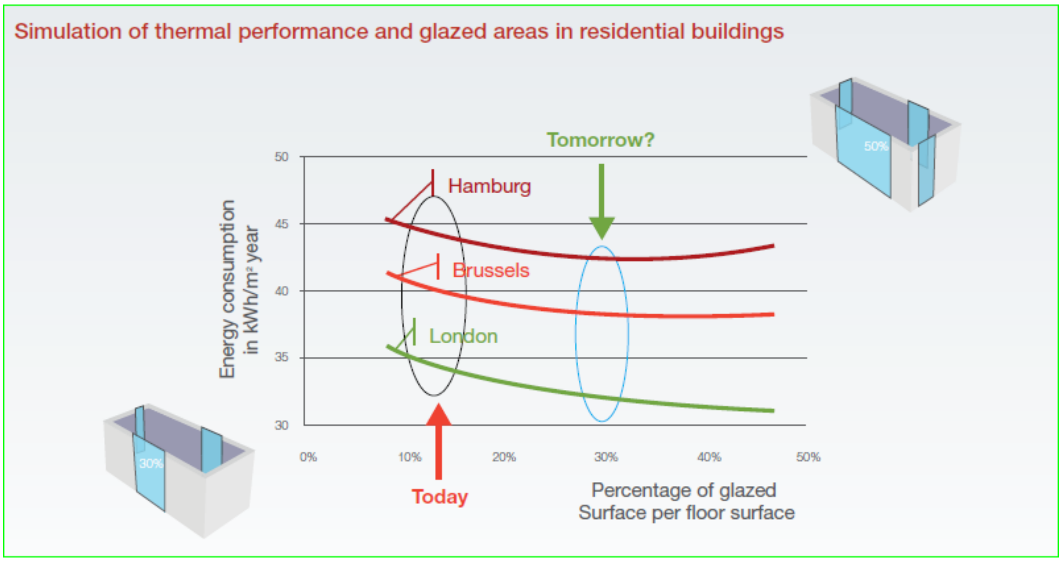

Figure 1 *In most climates enlarging size of high-performance windows helps to reduce energy consumption [3]*

TYPES OF SMART GLASS

Smart glass is composed of two major segments:

1. **Passive smart glass**: does not involve an electrical stimulus. Rather, it reacts to the presence of other stimuli such as light (Photochromic Glass) **(PC)** or heat (Thermochromic Glass) **(TC)**.

2. **Active smart glass**: it is also named switchable glass, and it changes its light transmission properties when voltage is applied. There are three primary types of active smart

glass technologies, each type with its own unique performance characteristics; Electro-Chromic devices **(EC)**, Suspended Particle Devices **(SPD)**, and Polymer Dispersed Liquid Crystal devices **(PDLC)**. These technologies are not one-constituent materials, but consist of multi-layer assemblies of different materials working together [5].

Photohcromic Glass (PC)

That changes color when exposed to light, Photochromic materials absorb radiant energy which causes a reversible change of a single chemical species between two different energy states, both of which have different absorption spectra. Photochromic materials absorb electromagnetic energy in the ultraviolet region to produce an intrinsic property change.

Thermochromic Glass (TC)

That changes color due to temperature changes. Thermochromic materials absorb heat, which leads to a thermally induced chemical reaction or phase transformation. They have properties that undergo reversible changes when the surrounding temperature is changed.

Electrochromic devices (EC)

Electrochromic windows center around special materials that have electrochromic properties. "Electrochromic" describes materials that can change color when energized by an electrical current. Electricity kicks off a chemical reaction in this sort of material. This reaction changes the properties of the material. In this case, the reaction changes the way the material reflects and absorbs light.

In electrochromic windows, the material changes between colored (reflecting light of some color) and transparent (not reflecting any light). Electrochromic glass provides visibility even in the darkened state and thus preserves visible contact with the outside environment. Electrochromic windows darken when voltage is added and are transparent when voltage is taken away. Like other smart windows, electrochromic windows are made by sandwiching certain materials between two panes of glass [5] (Figures 2 and 3).

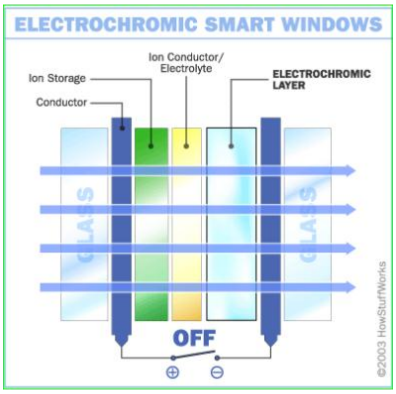

Figure 2 *EC when switched off [6]*

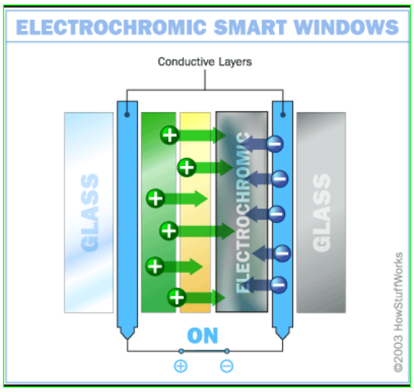

Figure 3 *EC when switched on [7]*

Suspended Particle Devices (SPD)

In Suspended Particle Devices (SPD), a thin film laminate of rod-like particles suspended in a fluid is placed between two glass or plastic layers, or attached to one layer.

When the power supply is switched on, the rod shaped suspended particle molecules align, light passes through and the SPD Smart Glass panel clears. When the power supply is switched off the rod shaped suspended particle molecules are randomly oriented blocking light and the glass panel looks dark (or opaque), blue or, in more recent developments, has a grey or a black color. SPD can be dimmed, and allow instant control of the amount of light and heat passing through. SPD window consists of several layers [5] (Figure 4).

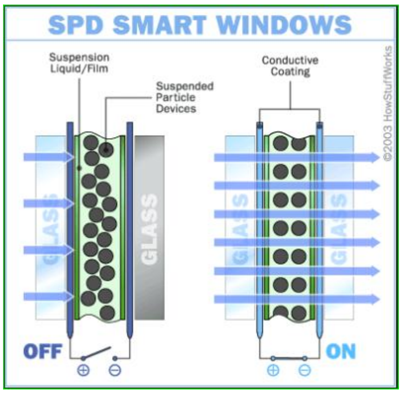

Figure 4 *SPD when switched off and on [8]*

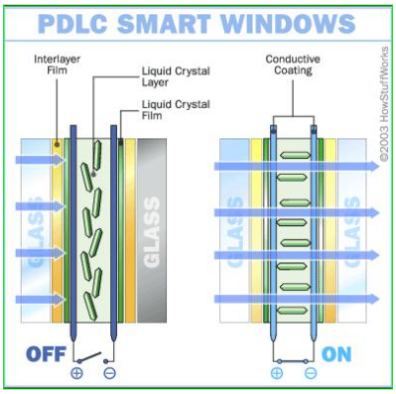

Figure 5 *PDLC when switched off and on [9]*

Polymer Dispersed Liquid Crystal Devices (PDLC)

In polymer dispersed liquid crystal devices (PDLC), liquid crystals are dissolved or dispersed into a liquid polymer followed by solidification or curing of the polymer. Typically, the liquid mix of polymer and liquid crystals is placed between two layers of glass or plastic that includes a thin layer of a transparent, conductive material followed by curing of the polymer, thereby forming the basic sandwich structure of the smart window. The degree of transparency can be controlled by the applied voltage [5] (Figure 5).

BENEFITS

Generally there are a lot of benefits of using smart glass (Table 2).

Table 2 *Wide benefits of using smart glass in smart windows comparative with conventional windows [1]*

Conventional Window with Static Tint and Interior Blind/Shade	Smart Window
Static window tint degrades view to outside during low/no-sun periods	View to the outside is optimized even during low/no-sun periods
Partial shading from interior blind obstructs view	Variable shading does not obstruct view
Space consumption is relatively high	Space consumption is relatively low
Shading/privacy requires manual effort to close blinds or activation of expensive motorized shade	Sensors adjust light conditions automatically; manual light-control is as simple as turning a dial
Occupants less likely to control/optimize light levels	Ease-of-use and integration with sensors optimizes light levels
Daylighting benefits are not optimized	Daylighting benefits are optimized

APPLICATION IN ARCHITECTURAL DESIGN

So far, adoption of smart-glass windows has been most prevalent in office buildings, hospitals, and universities. Some of the facilities that are installing or have installed automatically tinting smart-glass windows in just the past couple of years include Overstock.com's new headquarters in Salt Lake City; a new Humber River Hospital building in Toronto; the Donna–Rio Bravo Land Port of Entry on the U.S. side of the Texas-Mexico border; a new dining hall on the campus of Southern Methodist University in Dallas; and the Mall of America in suburban Minneapolis, which has added a smart-glass atrium skylight as part of its expansion.

While the single-panel glass curtain wall in the lobby of **Boston's Museum of Science** provided views of the Charles River basin, the light from a low-angle sun reflected deep into the museum, and guests did not appreciate the glare. SageGlass was viewed as the best solution. The electrochromic glass tints automatically during changing light conditions, so museum visitors can get glare-free views. Three horizontal zones in the curtain wall blend the daylight. The glass also blocks sunlight on hot days, reducing energy demand (Figure 6) [10].

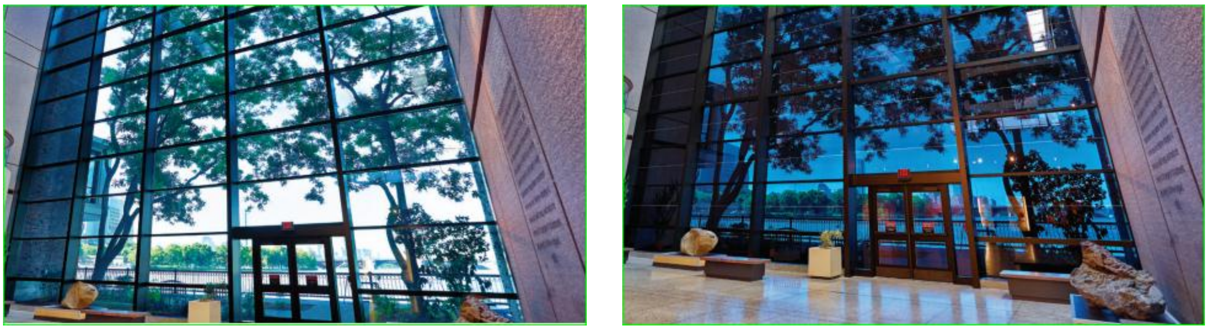

Figure 6 *SageGlass solves solar glare problem at Museum of Science, Boston while preserving the view of the Charles River [10]*

The rooftop garden terrace at Philadelphia's Kimmel Center for the Performing Arts offers striking views of the downtown Center City, but the open-air space became sweltering and unusable during some days because of heat from sunlight pouring through the center's barrel-vaulted glass roof. To help solve this problem, the building's owner and architect enclosed the terrace with dynamic glass panes (Jeffrey Totaro) (Figure 7) [11].

Figure 7 *Garden terrace at Philadelphia's Kimmel Center for the Performing Arts offers[11]*

Figure 8 *The ballroom in the Lory Student Center on the campus of Colorado State University[11]*

One advantage offered by smart-glass products is the ability to tint different windows at different levels, depending on the amount of heat and glare being experienced. At a ballroom in the Lory Student Center on the campus of Colorado State University in Fort Collins, Colorado, the floor-to-ceiling windows on this day are set to three different tinting levels for a midday event (View Inc.) (Figure 8) [11].

The contrast between a clear view of the outdoors on a sunny day and the bluish tones of tinted smart glass is shown on a facade of the Helmerich Center for American Research at Tulsa, Oklahoma's Gilcrease Museum, which houses a collection of art and artifacts of the American West. When tinted, the glass blocks at least 97 percent of UV radiation, helping protect the collection from damage and fading (View Inc.) (Figure 9) [11].

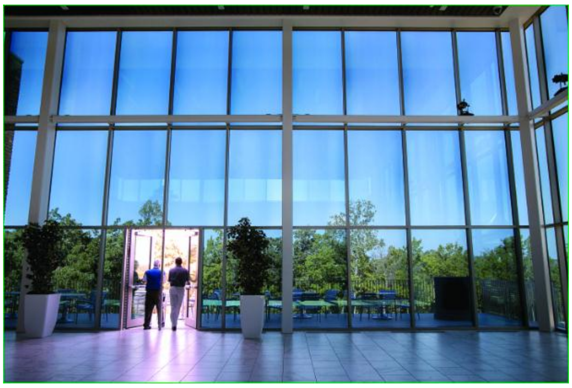

Figure 9 *Helmerich Center for American Research at Tulsa, Oklahoma's Gilcrease Museum [11]*

CONCLUSION

Architects are facing demanding challenges in designing, in order to satisfy the guidelines and regulations of energy efficiency of buildings. One of the solutions for meeting energy efficiency of buildings is usage of smart glass. Smart glass is a category of glazing materials that changes its light-control properties in reaction to an external stimulus making dwelling in the buildings comfortable 24 hours a day. It is used both for the public and individual buildings, on the facades and in the interior. Glass facades using smart glass technology reduce the need for air conditioning during the summer months and for heating during winter. Expectations for growth in smart glass demand are very high.

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ENERGY EFFICIENCY ANALYSIS OF THE MINING DEPARTMENT BUILDING-TECHNICAL FACULTY IN BOR

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Abstract

Negative ecological effects of irrational use of energy are topics with increasing attention in the world. Serbia, wanting to take a step with the developed countries, has adopted a set of regulations, recommendations and plans for improving energy efficiency. However, irrationality in the use of energy is present in most sectors in Serbia. Buildings i.e. energy consumption for heating, cooling, operation of the same, have imposed themselves as the largest consumers. Measurement with thermal imager detected that the losses on the Mining department building were related to windows, so the calculation of the amount of energy losses and the proposal of the measures for improvement was made.

Keywords: Energy efficiency, Buildings, Energy losses

INTRODUCTION

The world's energy consumption grows year after year. According to the report *BP Statistical Review of World Energy* for June 2017, energy consumption increased by 1% in 2016. This value is less than the observed 10-year average of 1.8%, but energy consumption in addition to all reduction measures continues to grow [1]. The growth of energy consumption, especially those produced by fossil fuels, increases CO_2 emissions, and in addition to economic, it also becomes an environmental problem. Great efforts are being made to reduce the consequences of energy consumption from fossil fuels and prevent climate change.

The Republic of Serbia wants to join the European Union (EU) and take a step for "energy-efficient" countries in the region that have adopted Directive 2009/28/EC [2]. Directive 2009/28/EC was adopted by the European Parliament and the Council and refers to the promotion of the use of renewable energy sources. On the basis of this directive, Serbia has adopted a number of laws, regulations and action plans in the field of energy efficiency [3]. They are committed to achieve, at the national level, the final energy consumption of 9% by 2020 compared to the 2008 consumption. It was found that energy is the most scattered in the field of industrial production and building [4], so the largest savings are possible in these areas. The energy efficiency of buildings become a burning issue that is getting attention to the world, national and local levels.

An estimate that 20-40% of the energy is spent in the world for heating, cooling, functioning of buildings [5]. Energy efficiency of buildings means all those measures that improve the energy characteristics of a building and achieve energy savings by keeping the same comfort or providing better ones. Measures can be defined as technical (heating, cooling, renewable, etc.), building (space isolation, replacement of carpentry, etc.) can refer to applied devices in the facility (energy saving bulbs, etc.). But they can be organizational and cultural in the sense of raising the awareness of employees and students about the importance of energy savings.

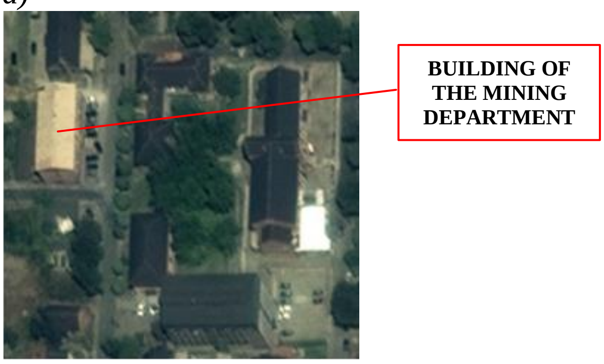
In the category of buildings dedicated to education and culture there is a large number of buildings built after the Second World War. These buildings feature a poorly energy-inefficient construction method, which is reflected in the deficiency of thermal insulation on the wrapper of the building and built-in already damaged out windows and doors. Due to all of the above, there is a large waste of energy that serves to heat and cool these buildings, while the comfort of staying in them is not satisfactory. For as much as that young people and children are staying in these rooms, it is necessary to improve the comfort of stay and achieve energy savings. The paper analyzes energy losses on the example of the cabinet in the building of Mining department of Technical Faculty in Bor, a proposal for measures to improve energy efficiency and energy savings has been given. Energy saving was achieved by replacing old windows with PVC doors and windows. A comparison of the heat loss analysis of one room with existing carpentry and analysis of thermal losses of the same room with the replaced and embedded new PVC windows is presented.

MATERIALS AND METHODS

Insight into the status of the Mining department building, from the aspect of energy efficiency

The facility is located in Eastern Serbia in Bor at the address of the Vojske Jugoslavije street No. 15. The closer location is shown in Figure 1a, the building belongs to the complex of the Technical Faculty in Bor. Built in 1958, it was intended for residential purposes. It was adapted for the needs of education in 1969. when the third floor was added. 1975. an extension of the Rock mechanics and soil laboratory was performed and an adapted roof construction, ie, a slanted roof with ASB boards was made [6]. The building has four floors and its height is 12m, while the height of one floor is 2.4 m. The building has a total surface area of the floor 416 m^2. All premises in the building are heated and the total volume of the building is 3500 m^3. The elevation of the building is 411 m. The object is oriented in length in the direction of North-South, so that the front facade is facing towards the east, shown in Figure 1b. All four facades are free and there are no objects in the area that prevent exposure to the dominant winds of this region. There is low intesivity exposure to winds, winds from E, W-NW, NW and W are dominant.

a)



b)

Figure 1 *a) The position of the building in the plan; b)Front facade of mining department building*

The first two floors of building are made of solid bricks (25x12x7cm), which both sides are covered with a cement mortar of 1.5÷3cm thick, shown in Figure 2a. The total thickness of the wall is 27÷28 cm. The third floor of the building is made of hollow blocks and the external facade is also made of mortar. The floor structure of the building is constructed as a semi-assembly structure with ribs shown in Figure 2b.

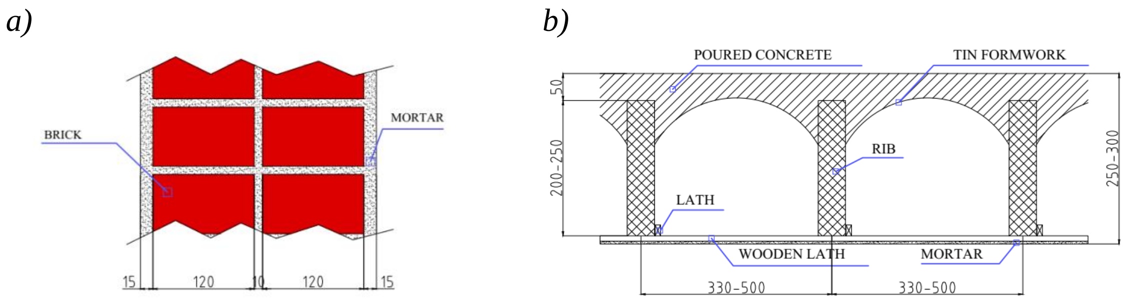


***Figure 2** The appearance of the cross-section: a) of the outer walls; b) interconnected structures*

Except for double-leaf front doors, the other doors in the building are made of solid wood. The building has built-in wooden windows, single and double winged windows, with one or two frames, windows are of poor characteristics and poorly sealed. A detailed overview of the built-in windows is shown in Table 1, the table shows that the total area of the window opening is 156.26 m^2. The total surface of the external construction of the building is 850 m^2, with 15% of the surface of the covered windows and doors.

***Table 1** Specification of windows of mining department building*

Windows	Three-wing single	Three-wing double sided	Double-wing and double sided	Double-sided (front)	Double sided (side)	Balcony door	Single
Number	2	30	10	5	6	10	14
Dimensions [m]	1.5x1.6	1.8x1.6	1.3x1.6	1.2x1.2	1.2x0.9	0.8x2.0	0.8x1.3
Surface area [m^2]	4.80	86.40	20.80	7.20	6.48	16	14.56

One-pipe heating system is designed for the facility. The pipe network in the heat substation is made of steel seamless pipes. The heating system is connected, via a heat substation, to the district heating system of Toplana Bor. Individually in the classrooms there are local air-conditioning devices. The outdoor units are mounted on the outside facade. The interior units are a wall type, there are a total of 12. The premises in the building are used on weekdays from 08.00 to 20.00, Saturday and Sunday only exceptionally. In the office and classroom can be present 25 employees and between 40 and 110 students [6].

Heat losses

The required amount of heat for heating is equal to the heat supplied to the environment. This amount of heat is called heat loss in everyday engineering practice. Heat loss is easily detected by thermograph recording using a infrared thermograph camera. Thermograph cameras are used for contactless recording of the temperature distribution of a body. They are developed for night vision and observation in poor visibility conditions. They are widely used in industry to control the accuracy of electrical installations. They are also applied for thermal imaging for the purpose of energy audit of buildings. For the analysis of the energy audit of the building, the thermal FLIR E5 camera of the newer generation was used, the thermograph cameras characteristics are shown in reference [8].

Calculations of heat losses for the mining department building are presented in the paper based on the calculation of thermal losses for one room. Specifically for the teaching cabinet located on the second floor of the observed object. The room is limited to the three inner walls of the same structure. Behind the frontal wall there is a hallway, while both side walls of the observed cabinet create common walls with next cabinets. The next cabinets are located on the north or south side of the room and their designed internal temperature is 20 °C. Above and below the observation room are also cabinets with the same internal parameters of the thermal comfort, separated by the intermediate structure depicted by the Figure 2a). Since the internal design temperature of the analyzed room is 20 °C, there will be no heat exchange between it and next cabinets, as well as those located above and below it. The heat will extend to the corridor, where the interior design of the corridor is 18 °C, through the inner wooden door and the inner wall located on the west side. Also, heat transfer is carried out through the outer wall on the eastern side, towards the environment, where the outside air temperature for Bor is -15 °C [9]. On the outer wall there are three-wing double-glazed windows and they represent the main sources of heat loss from the observation room.

RESULTS AND DISCUSSION

Measurement of losses by a thermograph camera was carried out in March 2018. Due to the large difference in external and internal temperature, losses are easily detectable. Figure 3a shows the east facade of the building, from the picture it can be seen that the losses due to the poor thermal properties of the building cover and the losses in the opening, i.e. windows. Losses in the thermal cover of the building are higher on the last floor of the building, which is built of hollow blocks. From the measurements shown by the thermograph camera, can notice that the windows are one of the main sources of thermal losses. In Figure 3c is displayed a thermograph image of a triple-wing window on the east facade of the building, white areas of the greatest losses are clearly visible. The situation inside the building (Figure 3b and 3d confirm the observations from the previous Figure 3c. The losses caused by the poor thermal characteristics of the windows are present on the entire surface of the window and are shown in blue colours. On the thermal image (Figure 3b), we are also notice the green zone of losses due to poor sealing and other of the windows and thermal bridges on the internal parts.

One way of improving the energy efficiency of a mining department building is certainly replacement of the window, in order to show the amount of energy that can be saved, the calculation of heat losses has been made.

Heat losses calculation

Comparative heat losses calculation has been made between room with three-wing double-glazed wooden windows and the same room with the replaced and embedded new PVC windows. It is done according to Regulations on energy efficiency in buildings, Serbian Standard SRPS EN ISO 13790 [7].

For heat losses calculation, the double glazed, two-wing windows with three-chambered profile frame made of PVC with air fillings between the panes has been chosen. Selection was based on analysis of the heat transfer coefficient calculation of different type of windows, and its geometrical properties, shown in paper [9]. 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 Roloplast [10].

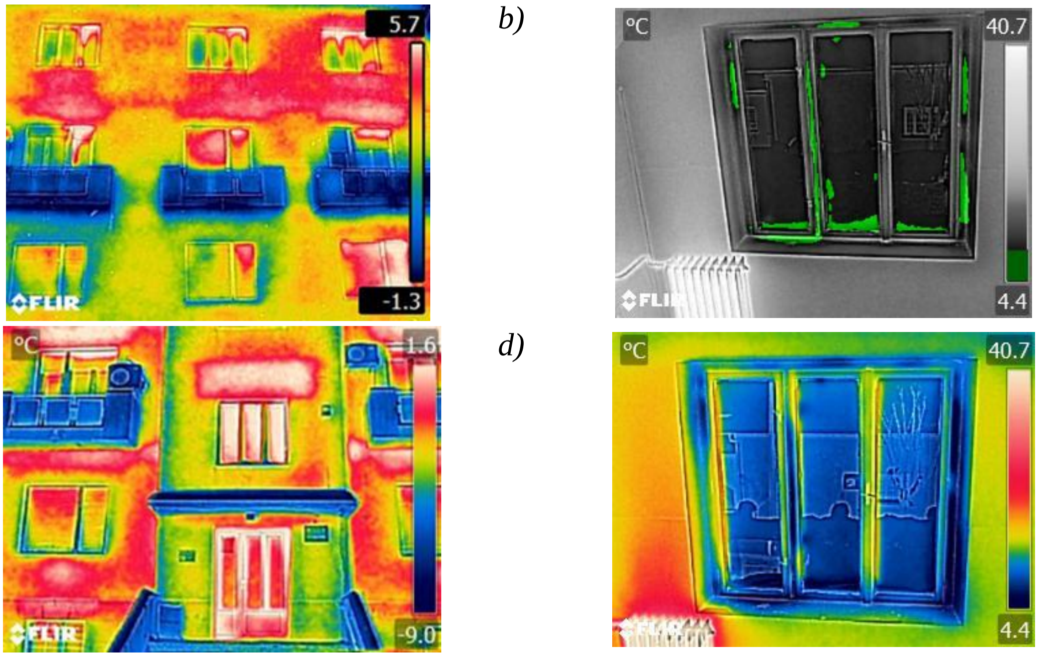


***Figure 3** Thermal image: a) East- facade of mining department building; b) three-wing single glass window; c) front facade of mining department building with windows; d) three-wing single glass window*

The heat that is transferred from the room to the environment or to rooms with lower internal temperatures is considered a heat loss. In order to achieve a satisfactory thermal comfort in the premises where people live or work, it is necessary to provide additional heat energy. Additional energy will compensate for heat losses, i.e. the amount of heat that is irreversibly lost from the heated room by transmission and ventilation.

Transmission losses represent the passage of a certain amount of heat transfer through the wall portion (windows) and the non-transparent wall. In order to calculate the transmission coefficient H_T, it is necessary to know the chemical and physical properties of the materials from which the walls, the wall structure, the thickness of the layers of the components from which the wall was built (Figure 2b). According to SRPS EN ISO 13790 standard, the annual energy required to compensate for thermal losses ($Q_{H,ht}$) according to the form is calculated:

$$Q_{H,ht} = (H_T + H_V) \cdot 24 \cdot HDD \cdot 10^{-3} \left[\frac{KWh}{a}\right] \tag{1}$$

where H_T, H_V are transmission and ventilation heat transfer coefficients, and HDD represent heating degree days.

Specific annual energy ($Q_{h,\,an}$) use for heating:

$$Q_{H,an} = \frac{Q_{H,nd}}{A_f} \left[\frac{KWh}{m^2\,a}\right] \tag{2}$$

where $Q_{H,nd}$ is annual required energy for heating and A_f is useful building area.

In order to save energy needed to compensate heat losses for a room where the heat transfer is carried out through the outer layer on the eastern side and the inside layer on the west side, the values of thermal losses with already existing windows and with the replacement of carpentry are calculated.

Table 2 *Annual energy required to compensate for heat losses and specific annual energy required for room heating*

	$Q_{H,ht}\left[\frac{KWh}{a}\right]$	$Q_{H,an}\left[\frac{KWh}{m^2a}\right]$
Wooden window frame	4702.34	185.6
PVC window frame	4551.14	178.2

Calculated values of thermal losses, ie annual energy required for compensation of heat losses, as well as the specific annual energy required for heating the analyzed premises of the observed object before and after the application of the optimization measure, ie, replacement of carpentry are shown in Table 2. In case of replacement of carpentry in the room, the energy savings necessary for the annual compensation of thermal losses of 151.2 KWh/a will be achieved, while the specific energy required for room heating is reduced by 7.4 KWh /m^2a.

CONCLUSION

The problem of energy losses in already existing buildings is omnipresent and requires large investment investments to be solved. These investments improve the energy efficiency of the building, which contributes to a more comfortable stay in them and environmental protection.

The paper analyzes the room with the most suitable position in the building for calculation of heat losses. i.e. the smallest heat losses, where the savings of the necessary energy for heat loss compensation of 4% per annum were achieved. It is expected that a change in the carpentry in the entire building will result in a much higher heat energy savings because the dry losses in other rooms are higher. Investing in exchange for worn-out joinery will affect the reduction of the heating bill for the building, and the investments will soon be reversed.

It is also necessary to consider investing in the insulation of the building and insulating the roof space because large heat losses are detected on the thermal image.

ACKNOWLEDGEMENT

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A NEW LONG-TERM SUSTAINABLE PUBLIC TRANSPORTATION SYSTEM FOR THE CITY OF SKOPJE

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Abstract

Skopje, the capital of Macedonia recently has been enlisted as one of the most air polluted cities in the World. A large portion of this huge pollution came from traffic, unorganized and unbalanced public transportation system currently based on diesel buses. In this paper, the authors propose a new, long-term sustainable public transportation system suitable for the city of Skopje based on the electric driven monorails, being focused on sustainability and clean energy. The proposed concept, its benefit along with the challenges, is briefly addressed. This research contributes to the literature as a pioneer study in Macedonia's academic work, along with its practical significance. Namely, it posts some valuable findings and suggests many recommendations that may serve as initiating ideas in the line of introduction of fast, reliable, massive, modern and ecologically friendly city transportation system.

Keywords: Public transport system, Monorail, Air pollution, Skopje

INTRODUCTION

Skopje, the capital of Macedonia with its total population of 506,926 inhabitants (2002 census) is one of the largest and most populated cities in the region. According to present estimations, the city of Skopje today has more than 650,000 inhabitants, and with daily inflow of almost 20,000 people, mostly for business purposes, it becomes one of the busiest and economically most valuable cities in the South-East Europe.

This results in life quality reduction, along with aggravated potentials for public transportation and commuting within the city. The thorny problem that the city of Skopje encounters is the traffic organization including reduction of traffic congestions, air pollution, and parking problem. With the gradual increase of its population, it becomes very difficult to commute from one to another part of the city in easy, fast and convenient manner. The streets became too narrow to accommodate the increased number of vehicles and the duration of so-called pick traffic hours sharply increased spreading almost over the whole working day. On the other side, these traffic problems along with the increased number of cars, buses and other transportation vehicles have a profound negative influence on the local environment. Additionally, due to its unfavorable geographical positioning being placed inside a large valley, the city of Skopje is highly susceptible to fog and keeping low-height clouds, thus dramatically increasing the air pollution, particularly during winter.

In the winter of 2018, the city of Skopje was ranked for several times at the unfavourable first place on the list of the most polluted cities in the World. It was noted over 374 $\mu g/m^3$ of PM_{10} and PM_2 particles, being almost ten times more than the critical values, and toping other largely populated and polluted cities like Kolkata (India) 361 $\mu g/m^3$, Dhaka (Bangladesh) 329 $\mu g/m^3$, or Lahore (Pakistan) 232 $\mu g/m^3$. Although not being the major, traffic is definitely one of the largest air pollution factors along with industrial plants and household heating facilities. The citizens of Skopje strongly demanded responsible institutions to undertake measures and activities significantly to reduce the air pollution, in the first line by decreasing the values under the critical. One of the potential solutions definitely is introduction of a new modern, ecologically friendly and long-term sustainable city transportation system that may replace the current system based on diesel-fuelled busses, being identified is one of the largest sources of air pollution in the city.

This paper elaborates a project idea of introducing a new sustainable city transportation model based on light and electricity driven monorail system [1-3]. In order to mean the aim, the paper is structured in several sections. The first section briefly explains the status of the current city transportation system putting an accent on its most prevailing problems. The second section, presents some stylized facts on the monorail transportation system, by discussing some major (dis)advantages along with supporting facts why such system might be suitable for the city of Skopje. The final section introduces a potential monorail structure which may be easily developed and expanded in accordance to the city's future needs.

PUBLIC TRANSPORTATION SYSTEM IN SKOPJE

The current public transportation system for the city of Skopje is run by the Skopje Public Transportation Company (**JSP** – **J**avno **S**oobrakajno **P**retprijatie). Some operational data for 2016 for this system are presented in Table 1, according to company's Annual Report [4].

Table 1 *Operational data for Skopje Public Transportation Company (JSP) for 2016 [4]*

Number of bus lines *(Urban/Suburban)*	**82** *(38/44)*
Transportation length [km] *(Urban/Suburban)*	**1,252** *(428/824)*
Yearly distance travelled [km]	**18,935,970**
Urban area / Suburban area	*11,379,926 / 7,556,044*
Total number of passengers per year	**45,925,737**
Average number of passenger per month	*3,827,144*
Average passengers per hour	*7,070*
Total number of busses	**428**
Average age of the busses [years]	**10.09**
Average consumption of diesel fuel per year [l]	**7,764,418**
monthly / daily	*647.035 / 21.214*
Average achieved commercial speed [km/h]	**19.47**
Average price per ticket	**0.55 $**

Based upon Table 1, it is noticeable the significant number of bus lines, transportation lengths and passengers. The age of the buses and diesel fuel spent daily, monthly and yearly is also very high, being a serious indication for substantial negative environmental implications. The average achieved transportation speed (< 20 km/h) is extremely low, generally due to narrow streets and congested traffic. This provokes significant unfavourable impacts on the interest for using the current transportation system (average 7,070 passengers per hour), despite the low price which usually does not cover full operating costs. Consequently, this leads to necessity of introducing changes in the transportation system for the city of Skopje, which will be focus on sustainability and clean energy.

Up-to-date, various models for new city transportation system have already been discussed, such as the gasification of the buses and/or procurement of new electric buses, up to introducing trolleybuses or even trams. However, so far, no model has been introduced or even deeper investigated. Some are just make-up solutions (gasification), others are not suitable due to existing overcrowded city structure and its geographical characteristics (trams), or their implementation needs totally new and expensive infrastructure that leads to additional traffic congestions (trolleybus and tram). Introduction of a subway was quickly rejected due to extremely high investment cost and lack of feasible number of passengers (needs > 20,000 passengers/hour) to justify such high investment costs [1] (Figure 1a).

Consequently, this leads to only two possible solutions: 1) Replacement of the current diesel buses with new electric or hybrid ones, or 2) Introduction of modern system for massive city transportation, like monorail or **LRT** (**L**ight **R**ail **T**ransit) system. The biggest obstacle for model based on simple substitution of the existing diesel-fuelled buses with electric ones is that the transportation infrastructure would remain still crowded and the transportation capacity could remain unchanged. Increasing the number of buses to achieve higher number of passengers, simply leads to increase of current traffic jams. Thus, in order to achieve long-term sustainable, fast, reliable, massive and environmentally acceptable public transportation system, although initially more expensive, one may prefer introduction of monorail or LRT transportation system over simple bus swaps. Even more, the number of passengers that may be carried at the same time, along with the flexibility of interconnection, is much larger when using monorails or LRT compared to buses. Since LRT transportation system requires heavy construction work and installation of double rail tracks, thus leading to additional narrowing of the available traffic space, this paper argues the introduction of monorail. Thus, this research proposes monorail transportation system as the most suitable, modern and long-term sustainable massive public transportation system for the city of Skopje.

WHAT IS MONORAIL PUBLIC TRANSPORTATION SYSTEM

Monorail (**MR**) is a modern, economical and environmentally friendly, fast and widely-used way for urban transport, particularly applicable for large city environments. Many countries worldwide apply this way of urban transport due to many advantages that it has. Today, such systems are widely used in almost all major world cities in the United States, Japan, Germany, Australia, France, Sweden, South Korea, Taiwan, Canada, China, etc.

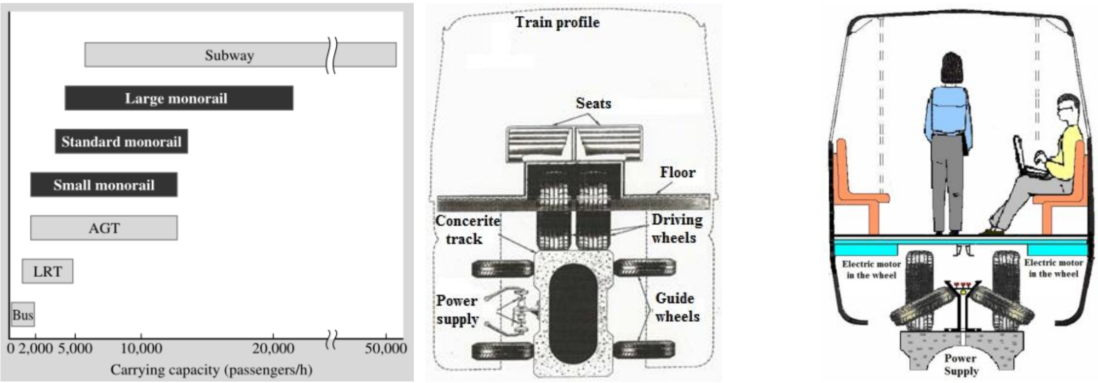
From a technological viewpoint, the MR may be considered as long electricity driven bus that moves along a single rail above the ground. MR tracks are usually not more than half the width of the vehicle, which means for safety reasons, a monorail vehicle has to be internally stabilized to prevent its lateral overturning. Thus, due to its narrow rails, these systems provoke less negative economic and environmental impacts compared to light or heavy rail systems. Commercially, there are three major MR types:

1. **Monorails that envelope/straddle a track.** A typical and most applied MRs worldwide concept named Alweg Monorail or Straddle Monorail, because it envelopes and straddles a narrow deep track. It is supported by two bogies and is guided by rows of stabilizing rubber wheel along each side of the track (Figure 1b and 2a).
2. **Monorails that run on top of a track or a slab at the surface.** A typical example of new MR technology comes under trade name Urbanaut®, which has a unique central guide rail on top of the track that prevents uplift and derailment of the vehicle (Figure 1c and 2b).

3. **Suspended monorails** under a track which is above the vehicle and the propulsion motors and bogies are on the top of the vehicles (Figure 2c).

Construction of elevated MR transportation structure may provide several major advantages, such as:

1. Elevated above the ground, MR occupies less space, provides better traffic safety, and it is faster and more secure;
2. Construction of MR driving system has a close resemblance to bus construction, meaning it is quite cheap, easy operational and straightforward for maintenance, and since it uses concrete or metal tracks, provides fast, fairly cheap and simple driving;
3. Due to electrical driving system, MR is almost noiseless, environmentally highly acceptable and recommended for very densely populated central city cores, thus avoiding collisions or traffic accidents;
4. MR is ***"green"*** thus saving lot of pollutant's emissions, which makes it advisable for densely populated areas;
5. MR may be easily accommodated within the current transportation system enabling transportation of people and goods directly in the city centre, using the so-called hide-in stations. The stations may be embedded in or side by existing buildings, shopping malls or any other facilities. All new stopping stations may get added-value by gaining inter-disciplinarily purposes like shopping, meeting and/or marketing places, etc., enabling passengers to get on/off the MR literally above the main street; and
6. Keep green areas under the tracks and among pillars enables environmentally friendly footprint of the facility. In this line, cars, people and any other traffic under the tracks may be unobstructed, meaning that the MR is actually increasing the space usage.



◆ *Transportation system capacity* ◆ *Straddle type* ◆ *Urbanaut® type*

Figure 1 *Transportation system capacity and vertical cross-section, and driving system*

a) *Straddle type* b) *Urbanaut® type* c) *Suspended type*

Figure 2 *Most common types of MR structures today worldwide*

WHY MONORAIL IN SKOPJE

Anybody who recently visited Skopje has the feeling that something must be done to improve the city transportation since the current is slow, inefficient and does not respond well to the city's needs. However, anybody could also ask, why MR should be selected as a model for future improvement of the city's public transportation network? We enlisted several major reasons that favour MR over other city transportation models:

1. Skopje is a 'flat' city being longitudinally aligned along the river Vardar. According to the latest census in 2002, the biggest municipalities are Gazi Baba and Aerodrom with over 72,000 inhabitants, Chair, Kisela Voda and Karposh with over 60,000 inhabitants and Centar and Gjorce Petrov with almost 50,000 inhabitants. In addition, it should be noted that these municipalities are located opposite to the Skopje city centre giving the opportunity for easy coverage with MR. Namely, with only two suitably designed MR lines with total length of about 16 km, one could accommodate almost 70% of all city public transportation needs;
2. Skopje has very unfavourable environment history, which means investing in environmentally acceptable long-term public transport is extremely useful. This should be promoted and supported by the Government, city authorities and various European environmental funds;
3. Skopje's geographical position divides it into central city area, industrial zones, and large "bedrooms" such as the municipalities of Aerodrom and Karposh, along with the international airport nearby;
4. Raising public transport above the ground level may release the current space for vehicles, new parking places, green areas and parks, bicycle track, etc., which may optimally improve the remaining transportation needs throughout the city;
5. Macedonia is heavily dependent on import of petroleum and natural gas, which instead of being used for transportation, it may be used more efficiently for electricity generation, thus enabling electrically driven MR transportation systems; and
6. Macedonia has good developed construction business, meaning that all operative may be successfully managed by domestic, local companies. In this line, all work in terms of foundations, track construction, stopping station erection works, etc. may be constructed with domestic input. Furthermore, the vehicles, power supply, as well as the control stations may also be produced by local companies supervised by international company fully experienced in development of MR transportation system, willing to transfer know-how and other knowledge. Like this, the local companies may obtain the necessary expertise which may lead to strengthening the economy by undertaking similar activities in neighbouring countries.

Proposed potential monorail lines

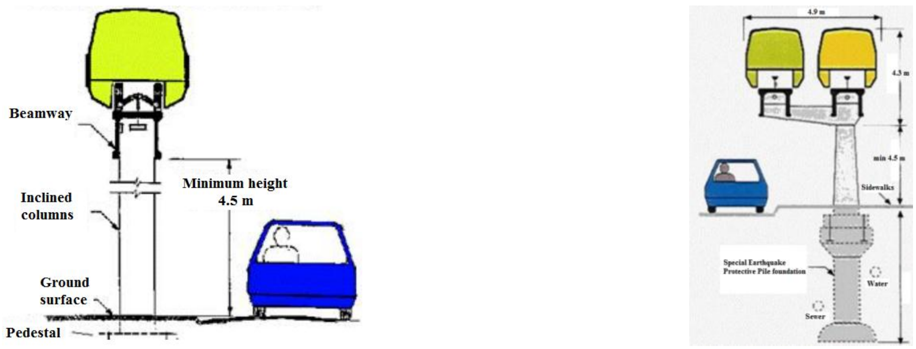
As previously mentioned, considering the city location, the number and location of potential passengers, the location of various important urban units, the proposed MR system may be initially constructed with two perpendicularly positioned lines:

1. **The Red Line** - from the municipality of Gjorce Petrov to Novo Lisice, with future potential line extensions to the municipality of Saraj and the recreation center Matka on one side, and Skopje International Airport on the other side, and
2. **The Blue Line** - from the suburbs of October 11, through Kisela Voda and the Koco Racin Boulevard towards the municipality of Chair and Butel, ending in the vicinity of the Skopje central Cemetery.

The economy of the project

The biggest challenge for such large-scale project as the MR is secure the financing. It is a common misconception that constructing something above the ground usually is very expensive, thus the MR system is far too expensive for countries in development like Macedonia. However, many countries that face similar problems such as traffic jams, over-crowded traffic and poor public transportation system, have made firm decision resulting in construction of public transportation system based on monorail technology. This is the evidence of China, Malaysia, Korea, and even Russia.

The construction costs for any MR structure depends on several factors. As the most important are: total length of the system, terrain topography, location and current utilities, passengers' requirements, speed, number of stopping stations, etc. The practice shows that almost 85% of the investment costs stand just for three items: civil works, monorails and/or special vehicles, and monitoring and control system [5,6]. Some insights of the construction costs for the Urbanaut® type monorail are presented in Table 2, while the vertical cross-section for the Urbanaut® monorail type I (single) and type II (dual) elevated systems are visually presented in Figure 3 [6].



a) *Type 1 (single line)* b) *Type 2 (dual line)*

Figure 3 *Vertical cross-section of the Urbanaut® MR system type I and type II with foundations [6]*

Table 2 *Typical cost for construction of Urbanaut® type monorail [million $/km] [6]*

Type of activity	Type I (single line)	Type II (dual line)
A. Elevated Guideways, Including Foundations	**3.20** (42%)	**5.85** (41.8%)
B. Passenger Loading / Unloading Facilities (2 Stations)	**0.75** (10%)	**1.20** (8.5%)
C. Maintenance Yards & Operational Control Facility	**0.50** (7%)	**1.00** (7.2%)
D. Electrical Power, Signals, and Moving Block Control	**0.45** (6%)	**1.00** (7.2%)
E. Rolling Stock (3 Single Vehicles or 3 Car Train)	**1.80** (25%)	**3.25** (26.8%)
F. Fees & Contingencies of A, B, C, & D	**0.75** (10%)	**1.20** (8.5%)
Total cost (Intermediate Size) *[million $/km]*	**7.45** (100%)	**13.5** (100%)

Based on findings in Table 2, some initial projection of financing is made. Accordingly, construction of two MR lines, as proposed for the city of Skopje, with a total length of approximately 16 km may cost between 120 (single line) and 220 (dual line) million euro. These lines will be the backbone of the whole future MR public transportation system. The suggestion is to be constructed as dual lines allowing passengers' commuting in both directions, as well as enabling further extension of the system with other single MR lines to other areas. In the first phase, all stations of the MR system should be well connected with other city's suburb areas that already have active bus lines. This will support utility and increase number of passengers for the MR system at least for additional 50%, thus achieving usage rate of more than 10,000 passengers/hour. This undoubtedly will improve the feasibility of the whole project. Therefore, the expected number of passengers may expand to approximately 65 million per year, allowing the average price of at least 1$ per single use. However, more detailed feasibility analysis are required, leading to financial justification, whereas, everything that may result in investments return rate under 12 years, is strongly acceptable.

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REGENERATIVE DESIGN AS AN APPROACH FOR BUILDING PRACTICE IMPROVEMENT

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Abstract

Conventional practice employed in building and infrastructure construction causes negative impacts on living environment, which are revealed not only in the initial stages but also through the entire life cycle. Negative effects related to significant energy consumption, and therefore, the emissions of harmful gasses, are the prevailing issue at the global level. In this regard, the aim of this paper is to point out the importance of the regenerative approach application when constructing new, and especially in renovating the existing buildings. Based on the analysis of various life cycle principles of building/built environment, the benefits of regenerative design application can be acknowledged. This approach, in principle, refers to acting in accordance with natural systems and processes. All stakeholders have to participate and contribute to the positive environmental effects through their activities and the use of contemporary technologies and systems.

Keywords: Life cycle flows, Regenerative design, Positive effects, Building renovation

INTRODUCTION

Benefits of modern urban settlements (such as housing, employment, education, health care, transport and other services) are indisputable; however, the construction and exploitation of facilities and infrastructure lead to significant resource consumption, emissions of harmful gases and generation of large volumes of waste. Given the situation, the question then arises as to whether the current development principles are suitable for use in future, taking into account the necessity to reduce the negative environmental impact and improve the quality of life. An analysis of conventional, contemporary and improved approaches based on the assessment of the life cycle of buildings and the built environment emphasizes the significance of choosing the appropriate methods to reduce negative environmental impacts and foster a multitude of positive effects.This approach is fundamental in the construction of new buildings, and is of particular importance for already built facilities especially in the exploitation phase in which negative impacts are prevailing, primarily due to energy consumption for air conditioning [1]. Buildings and transport sectors are the largest consumers of primary resources. These branches of industry are responsible for consuming 62% of energy on a global scale, as well as for 55% of greenhouse gas emissions [1]. In industrialized countries, the building sector accounts for 42% of total energy consumption, 35% of greenhouse gas emissions and more than 50% of primary materials extracted [1].

A comparative analysis of diverse approaches to design and construction has revealed the means to transform technical structures to mimic natural systems. Bearing in mind that, as a consequence of economic crisis, the proportion of newly constructed buildings is rather small - about 1.5% to 2% of the construction fund of the developed countries [2], and that 87% of existing buildings will be widely used until 2050 [3], the needs for renovating are getting bigger. Therefore, this paper considers the principles of renovating buildings based on the regenerative approach.

LIFE CYCLE – LINEAR FLOW

The Industrial Revolution, which contributed to colossal urban construction, was based on the so-called "linear flow" of materials and energy, since it was assumed that resources were abundant, accessible, easy to use, and that by-products could be simply and cheaply disposed of. In line with the development of industrial production and the introduction of new technologies, there has been a growing exploitation of resources, which intensified negative environmental impacts related to greenhouse gas emissions, air, water and land pollution, increasing waste generation, and pollution by chemicals and dangerous substances. Having in mind that natural resources are limited and that the production of materials and the exploitation of buildings and infrastructure are responsible for growing negative impacts on the environment which is not able to absorb all emissions and pollutants, it can be concluded that the linear flow of materials and energy in the construction of buildings/built environment is not a sustainable solution. The global awareness that one of the priority issues of humanity is the need to preserve and improve the state of the environment has matured, and the methodologies for assessing the environmental impact of a building/built environment life-cycle have been gradually developed in order to optimize the activities and their effects. Life Cycle Assessment (LCA) is a widely accepted scientific methodology that can be applied to identify, analyze and quantitatively assess the environmental impact of buildings/built environment [1,4]. There are two basic ways of setting the boundaries within the observed systems, particularly important for the implementation of the above activities: "from cradle to gate" and "from cradle to grave" [5]. A cradle-to-grave system assesses the impact of the entire life cycle of a building/built environment, whereas a cradle-to-gate system refers to industrial production, i.e. to the life cycle of the generation of construction products, from the extraction of primary materials to transportation of a finished product (Figure 1).

The LCA represents a significant contribution to better information within the decision-making process because it enables us to identify the potential negative environmental impacts by: 1) collecting data and making a life cycle inventory of all relevant energy and material inputs and outputs within the boundaries of the monitored system; 2) estimating potential environmental impacts associated with defined inputs and outputs from the previous step; and 3) interpreting the obtained results in order to improve the decision-making process [4,6].

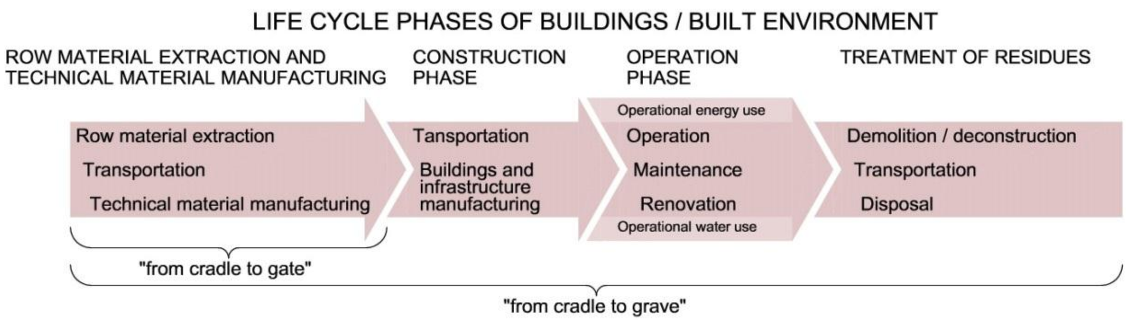

Figure 1 *A linear flow of the life-cycle of the building/built environment (adapted from [1,5])*

LIFE CYCLE – CYCLIC FLOW

A contemporary approach to environmental impact assessment involves the scrutiny over the final phase of the life cycle, or improving resource efficiency by considering the possibility to establish a cyclic flow in the "from cradle to cradle" model [5] (Figure 2). Within this approach, the possibilities of recycling and/or reuse of materials and elements have been analyzed in detail in order to reduce the negative environmental impact in comparison to the well-established practice of disposing residues to landfills.The cyclic flow, i.e. closing the loop, refers both to building design and construction in a way that allows the deconstruction, but also implies the growth of construction products that can be dismantled after their intended usage [5]. The described strategy is applied in the context of developing so-called green buildings which involve the improvement of various ecological characteristics in the entire life cycle.

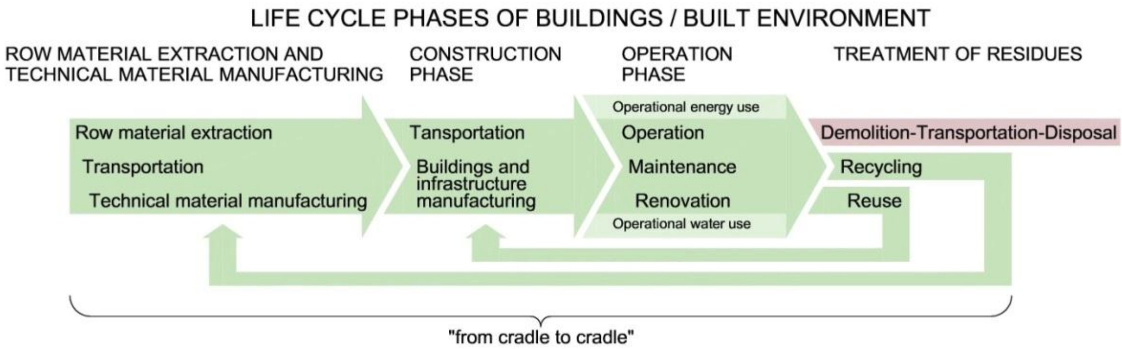

Figure 2 *A cyclic flow of the life-cycle of the building/built environment (adapted from [1,5])*

LIFE CYCLE BASED ON REGENERATIVE DESIGN

The application of LCA methodology discovers the opportunities for reducing the environmental impact of buildings/built environment and forming a cyclic flow model based on the cradle-to-cradle model. Ideally, most of these approaches tend to develop a zero waste system, but the question arises as to whether it is possible to develop a system with positive impacts on the environment. The answer is provided by the principle of regenerative design, that is, the integration of nature into a built environment. In regenerative design, nature and its models, systems and processes can be imitated or serve as an inspiration for solving urban problems related to the elimination of negative environmental impacts [7].

The concept of regenerative design extends the concept and the application of sustainability, by redefining the purpose of the built environment, the design process and the role of architects [8]. Although the application of green and sustainable design and construction supports the improvement of conventional techniques in terms of resource conservation and the mitigation of negative impacts on the environment and people, these approaches only slow down the degradation of natural systems which are invaluable for the provision of ecosystem services. On the other hand, instead of delaying negative impacts, regenerative design triggers a reversible process. In order to create urban systems that are mutually beneficial to both people and nature, it is necessary to establish interconnectedness among them. In this regard, regenerative design refers not only to architecture, but also to the activities of people that are parts of the system.

According to Lyle [9], the development of society influenced the process, in which natural systems of infinitely complex network of unique places adapted to local conditions and endless diversity, were replaced with a relatively simple, unified and generic urban system. In nature, the residues at the end of the life cycle of an organism are the primary material for the functions of others [10], and this is how a continuous, cyclic and self-renewing system is formed. Regenerative design supports natural processes which influence the rise of urban systems that tend to optimize rather than maximize their performances [8]. In this way, built environment becomes more resilient, which is one of the current issues of the contemporary societies.

Regenerative design is often comprehended as a return to nature and its cyclic flows, and the systems based on this approach have positive impact on the environment throughout their life cycles, as opposed to conventional, technical, "degenerative" systems (Figure 3) [10]. Conventional systems are characterized by linear flow and efficiency as their ultimate goal, whereas regenerative systems are the closed-loop structures with multiple pathways characterized by effectiveness, symbiosis, renewal capacity and integration with natural processes [10].

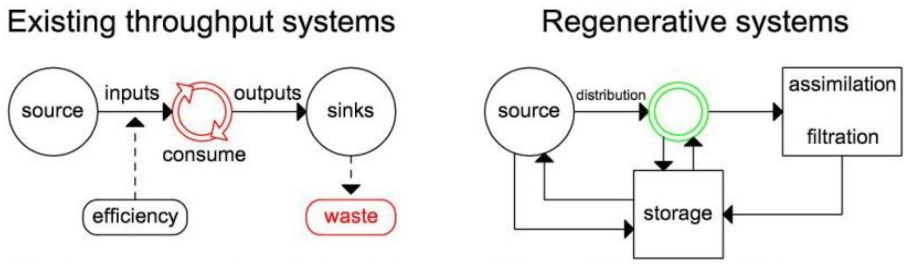

Figure 3 *Comparative view of the life cycles in degenerative and regenerative systems [10]*

RELATION BETWEEN DIFFERENT DESIGN AND CONSTRUCTION APPROCHES

The relationship between a conventional, green, sustainable and regenerative approach to design and construction is presented in Figure 4, as well as the impacts (both positive and negative) of the buildings/built environment on the environment during their life cycles [11,12]. Being strictly based on the construction of technical systems, a conventional practice does not consider the natural environment and demands considerable use of resources and energy in order to achieve efficiency. Such practice is often characterized as “doing things right”. A green approach, which contributes to slight improvement of the system, is defined as “doing less harm“. On the other hand, sustainable approach seeks to create neutral systems, that is, the systems without any negative impact on the environment. This approach is identified as “doing no harm“. By examining the upstream trend of an ecologically responsible design and construction, one can notice that apart from the regenerative approach commonly considered as the most efficient, the newly-introduced restorative and reconciliatory approaches refer to “doing good” for the environment. The distinguishing feature of these approaches is a scrutiny over people and activities that influence the system effectiveness. A restorative approach implies the role of people in the development of natural subsystems [12]. A reconciliatory approach perceives the human population as an integral part of nature, while in the regenerative approach humans participate as nature [12].

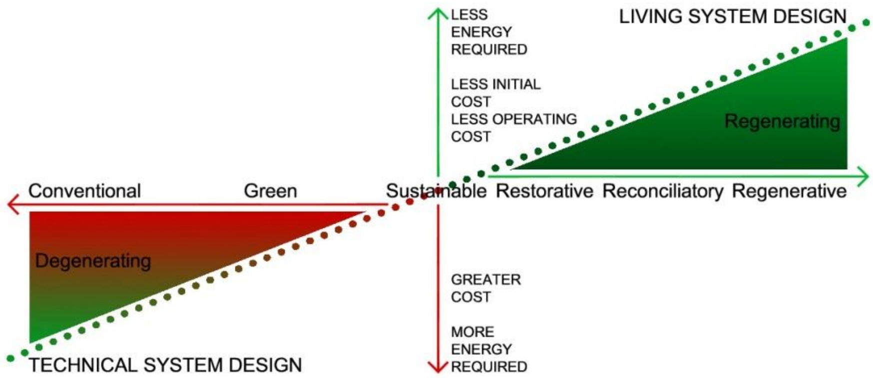

Figure 4 *The relation between different design and construction approaches (adapted from [11,12])*

POTENTIALS FOR EXISTING BUILDINGS IMPROVEMENT

In order to successfully renovate the existing technical systems/buildings in line with the regenerative approach, it is of primary importance to redefine the concept of the very building in terms of isolation from the external environment. The isolation of a building, as a significant requirement of modern architecture, is related to various factors and includes regulations and standards, the elements of entrepreneurial practice, marketing, users' interests and advanced technology systems [13]. Such a complex approach represents a current practice aimed to ensure sustainable development. Thermal comfort, which refers to balancing heat losses and gains and which demands a neutral environment, from a technical or engineering point of view, can be achieved by the complete isolation of a building and the use of air conditioning systems [13].On the other hand, an ecological or regenerative approach is based on a different comprehension of isolation and efficiency achievements. The buildings need to be designed in such a way that they are able to take as much solar energy, natural light, wind and water as possible. By applying modern technologies, renewable energy sources are transformed into new energies that could be used in building exploitation. Bearing in mind that the regenerative approach indisputably implies the implementation of living (green) systems, positive environmental impacts can be fostered by the application of technologies so that they become an integral part of the building, rather than the additional content [13].

Achievement of comfort causes significant energy consumption; however, in the early stage of new-building design, we can influence the reduction of energy consumption by choosing the form, orientation and volume. However, in case of the existing buildings these parameters are pre-defined, which emphasizes the need for renovation. General principles of regenerative approach have been presented on the example of a complete building renovation.

The new form of the existing building is the result of the removal of certain parts and the construction of the new ones, whereby all the requirements for integrating the building with nature have been fulfilled, especially those which refer to the use of natural processes aimed to achieve comfort and reduce the consumption of resources and non-renewable energy sources. Renovating ensures maximum exposure to natural light, natural ventilation and the collection of precipitation, and reduces the need for technical water (Figure 5a). The improvement was achieved by introducing a mechanical vertical communication system, by using the façades that control the flow of heat, light and humidity, as well as by the implementation of the green roof system, which provided an additional space for socialization and the possibility to create hybrid systems – a green roof and photovoltaic panels for energy efficiency (Figure 5b). Knowing that renewable energy sources are necessary for zero energy consumption, advanced technologies and systems are used with the aim to transform or filtrate energy into the desired quantity and form [13,14]. There are four possible systems, or their combinations, to use renewable energy sources – sun, wind, biomass and/or water (Figure 5c).

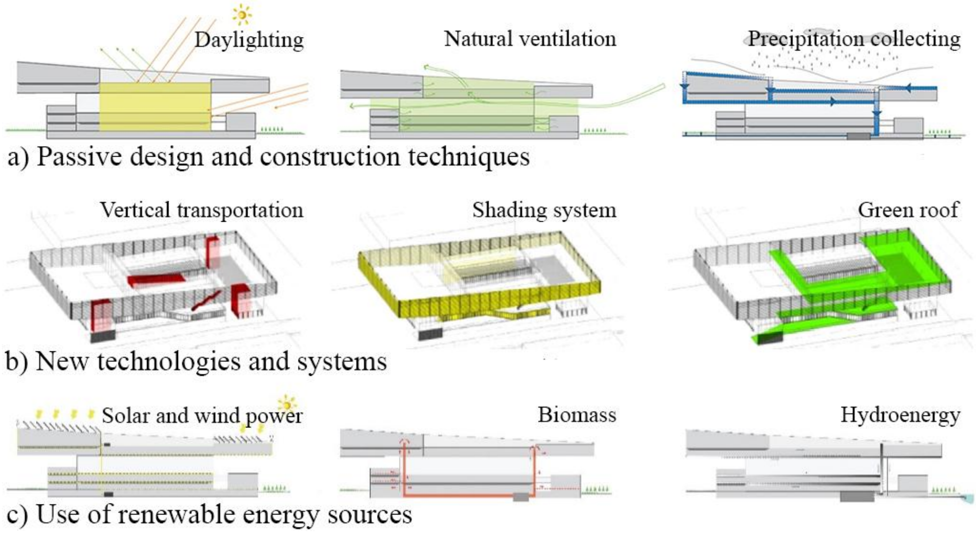

Figure 5 *The principles of renovating buildings by regenerative approach [14]*

CONCLUSION

The analysis of diverse approaches to design and construction, as well as their impact on the environment, points to the necessity and possible ways of improving architectural practice. Although full effects can be achieved if regenerative design is applied in a wider context of the built environment, each individual system is considered significant because each intervention within the building is a step towards the achievement of the set goals and objectives.

Due to already densely built urban cores, the existing building fund needs to be improved by applying regenerative approach. The complete renovation of buildings by regenerative approach, which relies on the use of passive design and construction techniques, the application of modern technologies and systems, and the activities of participants in line with natural processes, is a concept that should be implemented in the majority of existing buildings in order to achieve the desired outcome.

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ECOTOURISM CERTIFICATION PROGRAMS: MANAGING FINANCING

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Abstract

Ecotourism is a subcomponent of sustainable tourism and sustainable version of the primary tourism based on the nature, including various different elements of rural and cultural tourism in all its forms. The main intention is to achieve results and effects in terms of sustainable development. The paper gives a glance on financing ecotourism certification programs. In this line, it underlines the necessity of developing certified programs that measure different aspects of ecotourism. Moreover, the paper poses the general and specific objectives stated in the specific ecotourism accreditation program. The summarized findings present that small ecotourism enterprises lack financing along with missing appropriate information, technical capacity and capabilities to search for funding. More precisely, they are not sufficiently informed about the sources of financing ecotourism programs, and are not ready to take the debt without clear cost-benefit analysis. In this regard, one may assist them by creation of a public-private partnership in the field of ecotourism. Finally, the paper concludes that tourism businesses, which have identified the necessity of certifying ecotourism programs, needs unconditionally to follow standardized ecotourism principles.

Keywords: Managing financing, Ecotourism, Certification, Tourism development

INTRODUCTION

Being identified as a subcomponent of sustainable tourism, ecotourism includes persons or groups with very clear ecological mind, who participate in all activities and other possibilities settled in the environment. Yet, their increased number arise the issue of increasing infrastructural activities often being not sufficient. Some basic characteristics, which are mentioned at the concept of ecotourism and accommodation for which these tourists are interested in, are: (i) Well preserved areas; (ii) Using simple types of accommodation; and (iii) Strict adherence to the environmental protection, including limited number of visitors. Hence, the main intention of ecotourism is to decrease negative effects made by mass tourism.

In past decades, these efforts to validate the effects and success of ecotourism are still at an early stage. Given the fact that ecotourism is further defined by its participants and markets, many questions remain unanswered about how the success story of ecotourism can be verified. On the other hand, ecotourism business cannot be successfully run without investing in ecotourism certification program, which assists in surviving in the competitive tourism market, as well as in improving performance, and raising image and confidence of the company.

This research gives a glance on the importance of applying ecotourism certification programs. Moreover, it recalls some basic types and mechanisms for funding, by concluding that tourism, particularly ecotourism unconditionally needs to follow general and specific objectives and principles noted in the certification programs. In order to meet the research aims, the paper is structured in several parts. After the introductory part, the following section gives a brief overview on theoretical aspects of the certification programs in ecotourism. A snapshot on stylized facts on why certification is a need to tourism businesses is followed by a section briefly describing the phases how to certify the programs. The accent is put on the section presenting the main issues on managing finance on ecotourism certification programs. The article's final section offers the conclusion about the investigated issue.

LITERATURE REVIEW

There is a large pool of approaches towards the ecotourism certification programs. Yet, one is certain that all address specified criteria applicable to the working style of the entities involved in ecotourism development. On the other side, these programs are designed specifically for ecotourism or sustainable tourism in general, and have an urgent need to build international guidelines to address the task how to develop and manage certification programs. Bien [1] notes that certification is a way of ensuring that an activity or a product meets certain standards. Moreover, it is "a voluntary procedure that assesses audits and gives written assurance that a facility, product, process or service meets specific standards. It awards a marketable logo to those that meet or exceed baseline standards" [2]. According to de Vicente [3], certification has a much larger impact on supply side of the ecotourism market, than on the demand side.

Certification programs have dual role of increasing industry, firstly, performance by providing guidelines on how to be more sustainable, and at the same time by providing marketing benefits [4]. In this line, Klintman and Boström [5] mention internationally harmonized eco standards known as ecological standardization schemes. Some programs are even more legitimate for the so called "green political consumers" [6], or give the priority to certain criteria [7-10].

WHY CERTIFICATION?

Table 1 gives a glance on the importance of the certification process.

***Table 1** Certification benefits [1]*

Body	Benefits
Business	- Helps businesses to improve themselves; - Tends to reduce operating costs; - Enables easier access to the technical assistance and financing for businesses to implement new technology; - Ensures marketing advantage to certified businesses, as consumers learn to recognize credible certification brands.
Consumers	- Provides tourists with environmentally and socially responsible choices; - Increases public awareness of responsible business practices; - Alerts tourists to the environmental and social issues in an area, allowing them to act more respectfully or contribute to solutions; - Offers better quality service.
Government	- Helps governments to protect their market niches as ecotourism or sustainable tourism destinations; - Raises industry standards in health, safety, environment, and social stability; - Lowers the regulatory costs of environmental protection; - By requiring economic benefits to communities, it can help reduce poverty, especially in rural areas.
Local community	- Requires businesses to protect the environment and do little damage to it; - It requires businesses to respect local culture and provide real economic and social benefits for it; - It is likely to continue offering benefits for the long term.

Along, several additional reasons are noted for justifying the necessity of certifying tourism businesses, like: Improving quality and performance of their business and staff; "Doing the right things" to protect the environment and local community; Cutting costs; Gaining marketing advantage; and Avoiding being lumped with "green-washed" businesses that are not sustainable, yet try to claim to be [11].

HOW TO CERTIFY?

Getting certification program is not an easy process due to many open issues. One of the biggest limitations is its poor recognition by the consumers. Having in mind that this program type is applicable only to ecotourism products and not to general tourism businesses, it creates additional dilemmas in certification process.

Table 2 presents the key phases in certification program development, which are essential for establishing, developing and maintaining reliable certification program.

Table 2 *Certification programs phases [12]*

Phase	Steps
I Start Up	- Involve a multi-stakeholder body, consisting of representatives from government, tourism industry, academia, and non-profit organizations; - Conduct a feasibility study assessing market needs and readiness, funding sources, models of program structure and finance, etc.; - Develop a business plan; - Develop draft standards and procedures; - Finalize standards and procedures; - Establish audit and assessment protocol process; - Develop marketing materials; - Develop a monitoring and evaluation protocol; - Secure buy-in (and funding) from key interest groups.
II Operational	- Begin the process of assessing, auditing, and awarding businesses with certification label or logo; - Implement training and education programs; - Market program and certified businesses to tourism intermediaries; - Begin monitoring and evaluation.
III Consolidation	- Requires businesses to protect the environment and do little damage to it; - It requires businesses to respect local culture and provide real economic and social benefits for it; - It is likely to continue offering benefits for the long term.

FINANCING ECOTOURISM CERTIFICATION PROGRAMS

Obtaining ecotourism certification arise certain costs, which are not limited to short-term or nominated as direct costs, and they can be presented as in Figure 1.

The entire set costs include costs for certain changes and financial needs in terms of equipment and infrastructure, necessary to meet the requirements of certification program. Especially in times of major activities, one have to consider major investing, like installation of solar panels. Many times these costs are related to introduction of very sophisticated technology. However, the improvements within the company during the period of certification, leads to conclusion that these costs is expected to bring benefits in much bigger internal efficiency.

On the other hand, small ecotourism enterprises need to have smaller investments since they act in the limited environment and apply small range of technologies. But tight budgets, as well as the long-term financing costs represent big charges for the most of small ecotourism enterprises. They are at “pole position” not only in access to finance, but also in the implementation of any new system and technology that have or are required to be introduced.

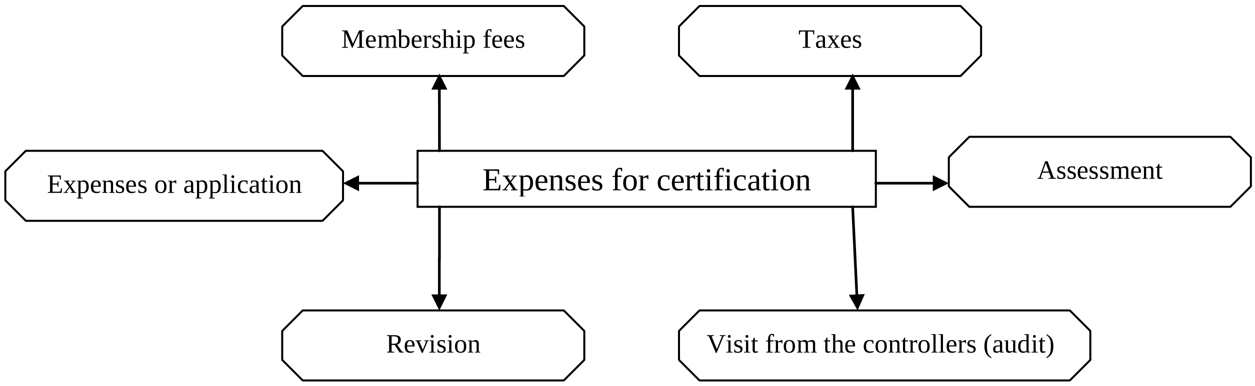

Figure 1 *Ecotourism certification costs [10]*

Therefore, small ecotourism enterprises do not have just lack of funds, but mostly lack sufficient information and technical capacity and capabilities to clearly understand the benefits and effects of ecotourism. Moreover, they:

(a) Do not know where to look for funding for their projects;

(b) Are not ready to take the debt without clear cost-benefit analyses; or

(c) Do not know how and where to seek for technical assistance for funding sources.

One approach to assist ecotourism entities is forming private-public partnership with other stakeholders active in ecotourism. These stakeholders (Government, NGOs, industry, donors, etc.), generally have some common interests in providing the highest standards. Hence, most of them are eager to meet the requirements of the certification program. Furthermore, they can play an important role in the overall means of providing technical and financial resources. The Government, for example, through subsidizing social and economic conditions necessary for meeting the certification program criteria for sustainable environmental development, may assist in great manner in sustainability of ecotourism.

Based upon Table 3, it is noticeable that costs for ecotourism certification are divided into two groups:

I Direct costs, which are directly related to the certification process (known as temporary or short-term costs). Generally, this group of costs includes: (i) Application of taxes; (ii) Acquisition of technical documentation; and (iii) Visiting from some agencies or consultants to implement the certification;

II Indirect costs, which are long-term, fixed and variable costs, and generally address: (i) Using the best available techniques; (ii) Education and training; (iii) Technical assistance; and (iv) Investments in infrastructural projects.

In terms of financing certification programs, tourism businesses may have in mind the following funding mechanisms:

- Financial instruments, such as: financial aid, subventions, grants, loans and payments for services which are performed in the environment, and so forth;
- Financial support i.e. direct or indirect subsidies such as cost reduction or other forms of financial support, like: (i) Informal taxes (membership, application, review, training, income, etc.); (ii) Reduced costs or loans from the government for small businesses to implement specific sustainable practices; and (iii) All types of support, including technical assistance to offset the investment needs and direct payment of subsidies from NGOs, donors and governments.
- Grants, usually used to cover the program costs for providing technical assistance and training programs;
- Loans and Loans guarantee;
- Other types of support, like: non-cash asset, technical assistance, marketing assistance or through business administration;
- Finance for conservation;
- Payments for the eco-environmental services;
- Other considerations.

Table 3 *Sample costs for certification programs [13]*

Type	Cost item
I Direct costs	Fees such as application and manual. Audit/Assessment costs: - Travel, food and lodging for auditors; - Daily rates for specialists or internationally accredited auditors; - Multiple visits: pre-assessment, diagnostics, audit, and verification inspections. Logo and licensing fees.
II Indirect costs	Costs of meeting certification requirements: - New management systems and technologies; - Investment in infrastructure; - Creating and maintaining management systems; - Staff training on implementing certification criteria; - Creating and maintaining social programs; - Creating and maintaining environmental programs; - Meeting and maintaining quality and service standards.

CONCLUSION

The paper gives a glance on the possibility to manage financing of ecotourism certification programs. It underlines the necessity of developing certified programs that measure different aspects of ecotourism. In this line, the paper found certified programs to ensure that ecotourism:

(i) Empowers local communities around the world to fight against poverty and to achieve sustainable development;

(ii) Provides effective economic incentives for conserving and enhancing bio-cultural diversity and helps protect the natural and cultural heritage; and

(iii) Promotes greater understanding and appreciation for nature, local society, and culture.

With regards to general and specific objectives stated in the ecotourism accreditation program, the paper found that around 80% of specific criteria must be fulfilled in order to get the certification. That means that more than 2/3 of each category (nature; interpretation; environmental sustainability; protection; working with local community; cultural component; customer satisfaction; and responsible marketing) must be met.

Finally, the research underlined the basic financial obstacles for tourism enterprises in the process of certification. Although the first impression is that small ecotourism enterprises have lack of funds, the practice showed that they are often faced with lack of appropriate information, technical capacity and capabilities to search for funding. More precisely, they are not sufficiently informed about the sources of financing ecotourism programs, and are not ready to take the debt without clear cost-benefit analysis. In this regard, the paper argues the possibility of creating a public-private partnership in the field of ecotourism. Referring the types and mechanisms for funding, the paper recalled numerous financial instruments for providing funds for certification of ecotourism businesses. So, subsidies, grants, guarantees, credit loans, non-cash assets and other funding sources are elaborated.

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SUSTAINABLE CITIES - ALBA IULIA, ROMANIA

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Abstract

Sustainable development is the concept promoting the conciliation between the socio-economic progress and the environment. It aims at meeting people’s present needs, yet without damaging the possibility of future generations to meet their own needs. The ongoing development of urban settlements has lead to a significant consumption of non-renewable natural resources and to pollution. Currently, authorities and city planners worldwide face the challenge of transforming urban agglomerations into „sustainable cities”, eco zones capable to ensure the survival only on green non-polluting energy. Several nations have legal provisions supporting such projects. Globally, there are numerous NGOs that have the same purpose, that is urban sustainable development. Romania is one of the European countries having a sustainable development strategy as well as a strategy for the capitalization of renewable energy sources. Thus, Alba Iulia has managed to become one of the 100 green cities in the world, and is a model for other cities in the country.

Keywords: Pollution, Sustainable development, Green city, Electricity, Renewable sources

INTRODUCTION

The desire to change and protect the environment comes with pollution and the crisis of natural resources. At the 1972 Stockholm Conference on Environment, they publicly acknowledge that human activities have caused environmental damage. It is only after 11 years that the World Commission on Environment and Development (WCED) is formed, following a resolution of the United Nations General Assembly. In the report of this organization, known as the Brundtland Report from 1986, entitled "Our Common Future", it is admitted that economic development cannot be stopped, but that its strategies can be changed, and sustainable development is defined as the one that pursues the needs of the present, without compromising the ability of future generations to meet their own needs. Another important moment in sustainable development is the Rio de Janeiro Earth Summit from 1992, which adopts the resolution known as Agenda 21, the document containing the basic principles of this type of development, a guide to the world's states.

At European Union level, the Sustainable Development Strategy adopted in 2001, and revised in 2006 supports this development. This long-term document is regularly evaluated and reviewed.

Romania, as a member of the EU, must take into account its policies, and thus has elaborated its own National Strategy for Sustainable Development in the horizons 2013-2020-2030 that was approved by the Romanian Government by Decision no. 1460 of 12 November 2008, and submitted to the European Commission at the end of the year.

One of the directions envisaged for sustainable development is to increase the efficiency of the use of electric and thermal energy and to identify and use other renewable sources for its production.

Non-renewable energy sources are fossil fuels (crude oil, coal, natural gas) and uranium ores (nuclear energy). Renewable energy sources include wind, solar, water (hydraulic, tidal and potentially osmotic), geothermal and biomass.

For the moment, those in the second category are less used, which is why the European Union specifies the need to implement renewable energy promotion schemes through Directive 2009/28 /EC on the promotion of the use of energy from renewable sources.

At Government level, there is the Government Decision no. 1535/2003 regarding the approval of the Strategy for the valorisation of renewable energy sources, Law 220/2008 for establishing the system for promotion of energy production from renewable energy sources, republished in 2010, as well as an Emergency Ordinance amending and supplementing Law 220/2008 to improve the legislation on the production of energy from renewable sources and to support the development of this sector.

The law in question has created the legal framework needed to expand the use of renewable energy sources by [1]:

- attracting in the national energy balance the renewable energy resources needed to increase the security of the energy supply and to reduce the imports of primary energy resources;
- stimulating sustainable development at local and regional level and creating new jobs related to the processes of valorisation of renewable energy sources;
- reducing environmental pollution by reducing the pollutant emissions and greenhouse gases;
- ensuring the necessary co-financing in attracting external financial sources, meant for the promotion of renewable energy sources, within the limit of the sources established annually by the law of the state budget and exclusively in favour of the local public authorities;
- defining the norms on guarantees of origin, applicable administrative procedures and connecting to the electricity grid in respect of the energy produced from renewable sources;
- establishing the sustainability criteria for biofuels and bio liquids.

Also in this law are the approved mandatory annual allowances of electricity produced from renewable energy sources benefiting from the Green Certificates promotion system for the period 2010-2020, namely 8.3% in 2010 and 20% in 2020. The green certificate is the title which attests the production from renewable energy sources and through which the Romanian state supports the investors in this field.

The EU Member States have taken note of the importance of protecting the environment and producing energy from renewable sources, especially in the context of annual global electricity consumption growth.

GREEN CITIES

Cities have become more crowded, polluted, energy-consuming and stressful places for their own inhabitants by the year, so the future solution would be their transformation into intelligent, environmentally and people friendly cities that generate sufficient income by rationally using the existing resources. According to the data provided by the United Nations, 1/2 of the Earth's population lives in cities, 80% of the global GDP is generated in cities, and 2/3 of the world's energy is consumed by cities as well.

The idea of having a green city is not a very recent date, initially it took into account the existence of several green spaces, gardens and landscaped parks, but with the passage of years, the reduction and the efficiency of energy was also taken into account, all for the purpose of increasing the quality of life.

In 2008, the European Commission created the Covenant of Mayors in order to engage and support mayors to meet the EU's energy and climate goals. Participants have undertaken to reduce their CO_2 emissions by at least 40% by 2030, to adopt an integrated approach to climate change mitigation and adaptation measures, as well as access to energy. This organization has expanded its activity since 2011 throughout the world.

A coalition of mayors and city officials called the Compact of Mayors appears in 2014 at the initiative of UN Secretary-General Ban Ki-moon and his special envoy for cities and climate change, Michael R. Bloomberg, who is committed to reducing, as much as possible, local emissions greenhouse gases, increase resilience to climate changes and track progress in a transparent manner.

The Global Covenant of Mayors for Climate and Energy took place in 2014 through the union of the Covenant of Mayors and the Compact of Mayors, newly established.

The Non-profit Carbon Disclosure Project (CDP) has a global measurement and information platform for cities, states and regions, companies and investors to manage environmental impact. Each city - type member of this organization must periodically fill in a questionnaire (self - reporting), which calculates the percentage of electricity generated from renewable sources in total electricity consumption. In 2015, there were 314 cities that made such reports, in 2016 their number was 533, and a year later, in 2017, were 570 cities. This demonstrates that more and more cities are concerned about replacing non-renewable sources with renewable ones to provide the necessary energy. The annual top of cities (Table 1), which provides more than 70% of its energy from renewable sources, shows that this is possible.

Table 1 *Cities that provide their electricity from renewable sources 2017[7]*

Country	No. cities
Australia	1
Brazil	45
Cameroon	2
Canada	5
Chile	1
Columbia	4
South Korea	1
Denmark	1
Ecuador	1
Switzerland	4
Iceland	2
Italy	2
Kenya	3
Mexico	1
Mozambique	1
New Zeeland	3
Norway	3
Panama	1

Country	No. cities
Paraguay	1
Portugal	5
Romania	1
Sweden	1
USA	4
Tanzania	1
Venezuela	1
Zimbabwe	1
Total	96

One can notice that the distribution of these cities is on all continents, in 26 countries, but most of them are in Brazil. Of the total of cities, around 40 operate with 100% electricity from renewable sources such as Burlington (USA), Basel (Switzerland), Reykjavik (Iceland), Ljubljana (Slovenia), Fave (Portugal), Bolzano (Italy).

Worldwide there is a tendency to change the mentality regarding global warming, pollution and renewable sources, which leads to an increase in the number of cities that focus on the use of energy produced from renewable sources.

ALBA IULIA – ROMANIA’S GREEN CITY

Alba Iulia is the seat of the Alba County, mentioned in documents since 1276, located at an altitude of 330 m, at 46°05' north latitude and 23°34' east longitude, in the south-west of Transylvania, Romania. The city enjoys a special landscape by being located in the interference area of the clay hills descending from the Trascău Mountains with the plains in the valley of the middle course of the Mureş River.

This city stretches over 103.65 km² and the resident population is 66.369 inhabitants.

The road distance to the capital of the country is 348 km, and to the nearest cities with international airport is 77 km from Sibiu and 98 km from Cluj Napoca.

This city has a rich history and a plethora of anthropogenic tourist resources that support tourism.

In 2008, the Alba County Council set up a non-governmental organization ALEA (White Energy Local Agency) in order to breathe a cleaner air. The sustainable energy development of the county through the efficient management in the field and the use of the energy produced from renewable sources is the main objective of this association.

Now, the Federation of Romanian Energy Agencies - FAREN has its headquarters in Alba Iulia, and here is the only representative office of the AER (Assembly of European Regions) in Central and South Eastern Europe.

In 2010, Alba Iulia joins the European Covenant of Mayors, and in the following year finalizes its Action Plan for Sustainable Development (PAED), which sets the target for 2020 to reduce CO_2 emissions in the city by 24%. The Covenant of Mayors set a new target in 2016 to reduce these emissions by 40% by 2030, and the Alba Iulia Municipality has accepted the new challenge.

According to the Energy Efficiency Law 121/2014 regarding the energy efficiency that aims to create the legal framework for the elaboration and implementation of the national energy efficiency policy in order to achieve the national increase objective for energy efficiency, in 2015, Alba Iulia drew up its Improvement Plan Energy Efficiency.

In the same year, the city joined ANERGO - the first regional energy observatory in Romania, established by the European programme DATA4ACTION within ALEA.

The actions taken in Alba Iulia in order to save energy and reduce CO_2 emissions are:

- the thermal rehabilitation of the blocks of flats;
- the increase of the energy efficiency of public buildings and educational institutions.

The actions undertaken in Alba Iulia regarding the production of energy from renewable sources are:

- the installation of solar power systems with photovoltaic solar panels mounted on public buildings with an installed capacity of 258 KWe;
- the use of hot water generation systems for the Olympic pool through thermal solar panels.

The actions that have taken place in Alba Iulia for energy saving, CO_2 emissions reduction and efficiency of public local transport are the:

- modernizing of the public lighting system;
- upgrading of the fleet of buses for public transport;
- additional installation of noxious filtering systems on fleet vehicles;
- implementation of an e-ticketing system and attraction through accessibility of a greater number of passengers to local public transport.

"SmartCity Romania" is a project launched by the Ministry of Communications and Information Society to use modern technology in cities to streamline traffic, improve public transport, the relationship of citizens with the public authority, living conditions and the health and education system, and reduce pollution and consumption of energy. Alba Iulia is the first city in the country to be partner in the new project, offering to test smart demo solutions. Alba Iulia Smart City 2018 is the pilot project that relies on the development of public-private partnerships to study the impact of technologies necessary to a smart city, a project to be implemented over the course of a year. They expect to test one hundred smart applications that will collect data and will be adapted according to investors’ analyses and citizens' responses.

All these actions in Alba Iulia aim to reduce pollution and the use of energy from renewable sources.

The results obtained from the measurements made in 2008 at this municipality's level are taken as reference. Thus, one can see (Table 2) which was the final energy consumption by sources of origin.

***Table 2** Final energy consumption in Alba Iulia in 2008- on sources*

Energy sources	Absolute value (MWh)	Percentage from the final energy consumption (%)
Diesel	93127	12
Petrol	77717	10
Natural gas	516134	67
Electricity	87323	11
Final energy consumption	774301	100

Source: Action plan for sustainable energy PAED of Alba Iulia, pg.8

Natural gas was the main source of energy for Alba Iulia in 2008.

Also important are the results on energy consumption for public street lighting, transport, buildings and CO_2 emissions in the same areas (Table 3).

Table 3 *Energy consumption on sectors and CO_2 emissions for 2008*

Sector	Energy consumption (MWh)	CO_2 emissions on domains / equivalent CO_2 (t)
Transport	170844	44216
Buildings	600696	164037
Public street lighting	2761	1935
Total	774301	210189

Source: Action plan for sustainable energy PAED of Alba Iulia, pg.9-10

The sector with the highest energy consumption is the one of buildings, and that is also because they have to be heated. CO_2 emissions were also associated with buildings, accounting for 78% of their total.

According to the PAED Monitoring Report, following the measures taken and the actions carried out in Alba Iulia, the final energy consumption decreased by 15.13% in 2016 to 657149 MWh, and the CO_2 emissions by 14.18% up to 180384 tons of CO_2.

The area of green areas in Alba Iulia has expanded from 67 ha in 2010 to 154 ha in 2016.

The measurements for atmospheric pollutants (AB 1 urban station - Lalelelor Street) have revealed their annual average level, as well as the fact that in Alba Iulia their level has not been exceeded. The most toxic gases measured in the city, according to the measurements provided by the White Environmental Protection Agency, did not exceed the hourly limit value for the protection of human health (Table 4).

Table 4 *Annual average level (2016) of atmospheric pollutants in Alba Iulia [5]*

Pollutant	Total validated data	% available data	Samples with concentration ≥	Average value µg /mc	Frequency of exceedance (%)
Nitrogen dioxide (NO_2)	8120	92.4	≥200µg/mc = 0	24.70	0
Sulphur dioxide (SO_2)	8096	92.1	≥ 350 µg/mc = 0	7.89	0
Carbon monoxide (CO)	8253	93.9	≥ 10 mg/mc = 0 (mobile average)	Maximum daily value of averages on 8 hours/year = 2,669	0

The daily limit value of 50 µg / mc of particulate matter was exceeded five times at AB1 station but without exceeding the maximum number allowed by Law no. 104/2011 - on ambient air quality (Table 5).

Table 5 *Level of particulate matter measured in 2016 by automated method [5]*

Pollutant	Total daily validated data	% available data	Samples with concentration ≥ 50 µg/mc (daily)	Average value µg /mc	Frequency of exceedance (%)
Particulate matter (PM_{10})	360	98.3	5	12.94	1.39

The target values for heavy metals (Nickel, Cadmium, Arsenic) were not exceeded in 2016 and the maximum annual admissible lead value was of 0.5 µg / mc (Table 6).

Table 6 *Annual average regarding the values of heavy metals in the atmosphere (2016)[5]*

Pollutant	Nickel (ng/mc)	Cadmium (ng/mc)	Arsenic (ng/mc)	Lead (µg/mc)
Annual average	2.587	0.322	0.316	0.007

It can be said that the air in the city is within the accepted norm and that its pollution is minor.

The efforts of the local authorities and the economic agents in Alba Iulia have had positive results, so the city currently uses 99% renewable energy, most of which (96%) comes from hydroelectric power plants, 2% is solar energy, and 1% is wind, respectively resulting from natural gas. This has made Alba Iulia the only city in Romania to be included in the top of cities that provide their electricity from renewable sources starting with 2017.

Continuing actions in Alba Iulia will result in maintaining in the clean cities that use renewable energy sources.

CONCLUSIONS

The relationships established between man and nature determine living and working conditions, but also the prospects for the sustainable development of society as a whole.

Economic growth leads to increased environmental pressure, and to the generation of waste and emissions of air pollutants, so it is very important to monitor them and use modern, non-polluting or low-polluting technologies.

The natural resources currently used in the world are, to a large extent, exhaustible and can create a major global crisis. At the same time, in the processes of their transformation into energy, even if a small amount of polluting elements is released, so efforts are being made to use the energy produced from renewable resources.

At international level, there are associations that promote the production and use of green energy that is, generated from renewable sources. Using such sources builds up social capital that leads to a rise in living standards of the present and future. There are already cities around the world that have succeeded in adopting this idea and ensuring their energy consumption, over 70% of alternative, renewable sources.

The city of Alba Iulia in Romania is an example for us that it is possible and that there is potential in the country.

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CHALLENGES OF TOURISM BUSINESS IN CONTEMPORARY WORLD

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Abstract
Tourism has the potential to empower communities and the sustainable tourism agenda needs to focus on how to bring this about. Considerable investments are required in communication and trust building between the actors in tourism. In this context, to make successful development of tourism, it is necessary to understand the importance of entrepreneurship and human resource management. Tourism businesses have been identified as an essential actor for creating jobs and growing the economy in general. Also there is an attempt to identify the constructs that influence the building of the high-quality entrepreneurship in tourism business as the need of accessing of finance to make this reality. The study undertaken aims to explore the immediate effects of accessing and using finance on the current context of tourism, highlighting the influences on the tourism business in Italy and Spain.

Keywords: Finance, Entrepreneurship, Tourism, Business, Benefits

INTRODUCTION

The role of tourism in the economic growth and to the progress of modern societies has become a common awareness in political authorities worldwide. For this reason many attempts are being made in order to develop tourism, being among the most important sectors of economic activity, to the benefit of their economies as quickly and as effectively as possible. The contribution of the tourist sector is beneficial for the country's economy due to its influence on the sectors other than the foreign exchange sector, including: the employment sector, the business sector, the income sector, the cultural sector and the fiscal sector. Also, there is a need to underline the essential meaning of international tourism and trade, which are expected to be quite dependant on the exchange rate regimes. The international trade is another argument commonly used to justify the exchange rate policy. In this sense, more fixed exchange rates are expected to promote international trade and tourism via reduced uncertainty in the international transactions. However, the empirical literature is not conclusive in this task. The evidence about the effect of the less exchange rate volatility on trade is mixed [1]. The results are very sensitive across studies, depending on the countries and periods considered.

LITERATURE REVIEW

An entrepreneurship quality measure is essential to develop because it could help focusing on the high-growth of small and new businesses, according to the researchers. This will help to identify a wide range of economic, social, policy, and firm factors that may affect the development of high-quality entrepreneurship. Also it will enable entrepreneurs to uncover the critical role of the high-quality entrepreneurship in economic growth and in rural development too. One of the synonyms for entrepreneurs is the fact that they innovate. In this way they create and employ [2]. Entrepreneurship is necessary for the creation of the new organization, and the construction of the new businesses. So, it plays a crucial role for the success of the economic growth and leads to business benefits.

Entrepreneurial individuals transform their entrepreneurial ambitions and qualities into actions. So, an organizational extension of the individual entrepreneurial actions and a behavioural manifestation of entrepreneurship could be identified in small firms [3]. In this way, another authors expressed that entrepreneurship quality is connected to the job creation in small tourism business and to the economic growth in general. New small tourism businesses contribute to the flourishing of entrepreneurship as important catalysts or actors in technological innovations; as agents of changes in market structure and competition environment, and as critical forces in the industrial restructuring and national competitive advantage upgrading [4].

High-growth and high-potential small tourism businesses have positive impacts on the economic growth. The possibility to understand entrepreneurship quality is very important in a way to discuss about the essential meaning of entrepreneurial leadership, market and marketing orientation, differentiation and tourism destination development. This will enhance accessing high-quality entrepreneurship in tourism industry. Growth in the tourism industry will bring benefits which will facilitate job creation [5].The government regards this as an opportunity to create employment and to bring in equality in the country's job market.

FINANCES FOR STARTING BUSINESS IN TOURISM SECTOR

The tourism industry has been identified as one of the key industries for driving economic development and economic transformation in developing countries. Some authors define entrepreneurial leadership as "leadership that creates visionary scenarios used to assemble and mobilize a „supporting cast" of participants who become committed by the vision to the discovery and exploitation of strategic value creation" [6,7]. So, owner manager has a vision for using all the potential from tourism industry. But in the most cases the biggest problem for starting business in tourism industry is the financing. The costs incurred before any funding is received must be paid up-front by the developer/project proponent. A funder does not want to pay for costs already incurred. This applies particularly to non-profits applying for grant monies. Most lenders require the developer/entrepreneur to contribute cash equity towards a new development project or expansion of an existing business. A loan to value ratio of 50% is not uncommon for banks lending to tourism/hospitality businesses. Similarly, many grant programs will not provide 100% funding coverage [8]. They require applicants to demonstrate evidence of other funding sources to match the grant funds being sought.

In more advanced developing countries, where there is reasonable progress in the fundamental institutions, tourism SMEs may still face challenges in accessing formal finance in the form of bank loans, guarantees, venture capital, leasing and so on. Loans extended to tourism SMEs are often limited to very short periods, thereby ruling out financing of any sizable investments. Moreover, due to high-perceived risks in SME loans, access to competitive interest rates may also be very limited. Finally, in many developing economies, banks prefer to lend to governments, which offer less risk and higher returns, crowding out most of the private sector from the financial system [9]. There are generally three main funding options that tourism businesses can choose from to raise capital: debt funding, equity funding and government funding [3].

There are various factors that influence the choice of businesses to use debt capital as a source of financing. Some of the main considerations are the repayment period, the interest rate and tax implications. In most banks and credit unions there is the option of speaking to a representative in their commercial banking or small business department. Some banks may even have a hospitality/tourism lending expert(s). There are two main types of loans available from financial institutions: operating loans and term loans. Operating loans (short-term debt financing) are typically short term and finance the ongoing day-to-day operations of a business (such as employee wages, purchasing inventory, raw materials and accounts receivable). Term loans (long-term debt financing) are generally granted for capital investments or acquisitions, and there is a scheduled loan repayment period. This may include the assets being financed, along with personal guarantees from the business owner(s) and any other assets owned by the business, such as land, buildings, equipment and leasehold improvements.

ANALYSIS, RESULTS AND DISCUSSION

The growth of tourism refers to the gradual evolution of tourism which is an important factor for the productivity of a country's economy. This is accomplished with the complete evaluation and the rational exploitation of tourism resources, with the increase of tourism productivity and its qualitative improvement as with its adjustment to the needs or desires of tourists. The role of tourism to the economic growth and to the progress of modern societies has become a common awareness in political authorities worldwide. For this reason many attempts are being made in order to develop tourism, being among the most important sectors of economic activity, to the benefit of their economies as quickly and as effectively as possible. The contribution of the tourist sector is beneficial for a country's economy due to its influence on the sectors other than the foreign exchange sector. Here are included, for example, the employment sector, the business sector, the income sector, the cultural sector and the fiscal sector. Also, there is a need to underline the essential meaning of international tourism and trade, which are expected to be quite dependant on the exchange rate regimes. The international trade is another argument commonly used to justify the exchange rate policy. In this sense, more fixed exchange rates are expected to promote international trade and tourism via reduced uncertainty in the international transactions. However, the empirical literature is not conclusive in this task. The evidence about the effect of the less exchange rate volatility on the trade is mixed [1]**.** The results are very sensitive across studies, depending on the countries and periods considered.

In addition, the study covers several countries and explains the impact of tourism on their economy. Also, the estimation which measured the effect of tourism in Italy and Spain is made.

Spain

Increased tourism expenditure leads to adjustments through a real exchange rate appreciation that reduce exports from other exporting sectors and increases imports. The exact effects on the different sectors are a result of positive and negative effects, so the actual results are difficult to predict without numerical simulation. The gain in welfare following a tourism boom was found to be relatively small. This is because tourist expenditure doesn't itself create value. That is done by factors that provide services for tourists. In the absence of tourism boom, these factors could be employed in other sectors. The tourism boom increases productivity of these factors, hence their wage, by increasing the possibilities of employment open to them. So the CGE model doesn't assess the importance of tourism in terms of what proportion from GDP is attributable to tourism. Also, the literature offers research which proof that reductions in the value of non-tourism exports and increases in imports offset the increased revenues from tourism [10].

Italy

As far as Italy is concerned, many studies suggest that a long run bi-directional temporal causality is assessed for international tourism and economic growth. When the economic impact of tourism is measured, it is found that only physical capital is influenced by economic growth, traditional exports and tourism in the long term. The findings also suggest the importance of physical and human capital accumulation in the process. Furthermore, it is also found that traditional exports Granger cause economic growth in the short-run. Consequently, there is a strong influence from exports to economic growth, since it exists in both short and long terms. It is observed that the economic growth driven exports mechanism is also valid.

The results for Italy are consistent with its economic history. A study explains that by 1950 Italy had become the world's third most popular tourist destination after the United States and Canada [11]. Between 1951 and 1965, tourism growth in Italy averaged 11.5% per annum, and tourism's share of exports rose from single figures to 19.3% [12]. During and after this period the international tourism scene changed dramatically as population growth and demographic changes, technological innovations and socio-economic developments encouraged international travelling and competition, and as tour operators began to invest heavily in the comparatively cheap coastal areas of the Mediterranean (e.g. Greece, Spain, Turkey). Also, some authors underline the fact that additional negative factors limited Italy's ability to attract tourists from the 1970s to the 1990s, such as Italy's lack of quality accommodation and transport services, negative publicity stemming from natural disasters and pollution, crowding and congestion in major tourist centers, or petty crime, among others [13]. Later on, the 1992 recession and the continued stagnation of the Italian economy created inflation in tourism. However the devaluation of the lira in September 1992, and the unstable political situations in the former Yugoslavia, the Middle East, Egypt, Turkey and Spain had positive impacts on international travel to Italy and promising projections were made for the period 1994-2000. So, the message is more than clear – tourism expansion has crucial role for long-run economic growth, and also, there is the importance of physical and human capital with respect to economic growth and tourism expansion.

Data and methodology

We use World Bank data from 1993 to 2012 to estimate the effect of tourism on the selected countries Italy and Spain. As a proxy variable for tourism we use tourist receipts, in the analysis we also include the exchange rate as proxy for international prices -REER (Real Effective Exchange Rate) and Air departures as a proxy for transport infrastructure which is of importance for the tourism industry and the development of the country. As a dependent variable in our models per capita GDP growth variable is used. We apply OLS regression with country effects and we estimate three models, and also we use Dickey fuller technique on the residuals from the first model in the OLS regression to check for the cointegration of the variables.

Definitions of the variables

Definitions of the variables that are being used in our models are given in the following Table 1.

Table 1 *Definitions of the variables*

GDP per capita growth (annual rate %)	Annual percentage growth rate of GDP per capita based on constant local currency. GDP per capita is gross domestic product divided by midyear population.
International tourism, receipts (% of total exports)	International tourism receipts are expenditures by international inbound visitors, including payments to national carriers for international transport. Their share in exports is calculated as a ratio to exports of goods and services, which comprise all transactions between residents of a country and the rest of the world.
Real effective exchange rate index (2005 = 100)	Real effective exchange rate is the nominal effective exchange rate (a measure of the value of a currency against a weighted average of several foreign currencies) divided by a price deflator or index of costs.
Air transport, registered carrier departures worldwide	Registered carrier departures worldwide are domestic takeoffs and takeoffs abroad of air carriers registered in the country.

Descriptive statistics

Descriptive statistics of the model is of importance which has first insight in the values of the variables and their statistical properties (Table 2).

Table 2 *Descriptive statistics*

Variables	Obs	Mean	Std. Dev.	Min	Max
GDP per capita growth (annual rate %)	106	1.361604	2.966469	-7.95	6.21
International tourism, receipts (current US$)	94	14.16819	9.142885	2.08	35.28
Real effective exchange rate index (2005 = 100)	114	4.581697	0.080826	4.39556	4.900076
Air transport, registered carrier departures worldwide	108	54.5	31.32092	1	108

OLS regression and country effect analysis

In this section we perform OLS regression on three models and we estimate cross-country effects. Three models are reported in the following Table 3. We estimate the following functional forms:

$$\gamma = \alpha + Tr + \eta + i + \varepsilon \qquad (1)$$

Where γ is the economic growth in per capita terms variable, α is the constant of the variable and are tourist receipts as percentage to export, Tr and η are the other two variables namely infrastructure variable and exchange rate. ε is the usual error term, that is white noise error term that should follow normal distribution $N(0{\sim}\sigma^2)$ for the estimated coefficients to be BLUE (Best Linear Unbiased Estimators) and i are the countries that we control for.

Table 3 *Regression results*

Growth of GDP per capita is dependent variable						
	(1)		(2)		(3)	
Independent variables	**Coef.**	**P>|t|**	**Coef.**	**P>|t|**	**Coef.**	**P>|t|**
Tourism receipts	0.35	0.14	0.51	0.04	0.44	0.09
Exchange rate			-2.76	0.05	-2.85	0.04
Air departures					0.18	0.16
Spain	0.75	0.16	0.61	0.25	0.45	0.41
Italy	0.50	0.13	0.12	0.76	0.11	0.77
Constant	-0.33	0.68	12.17	0.05	12.09	0.05
Functional form (p-value)	0.0224		0.1921		0.2694	
R^2	0.2542		0.3023		0.3272	

From the results we can observe that tourist receipts are positive and significant or nearly significant, especially with the influence of exchange rate. Exchange rate influences negative and statistically significant on the economic growth per capita, as infrastructure variable signs on the exchange rate variable and air departures are as expected, while infrastructure exerts positive relationship with economic growth (Figure 1 and Figure 2).

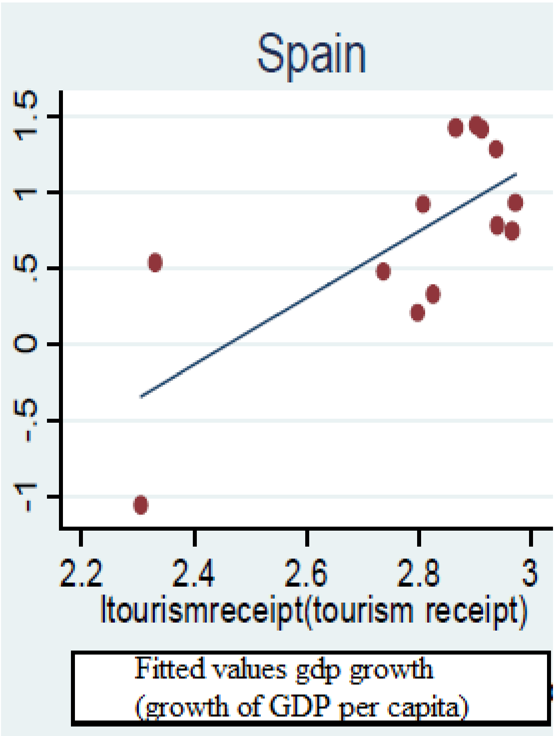

Figure 1 *Growth of GDP per capita (Spain)*

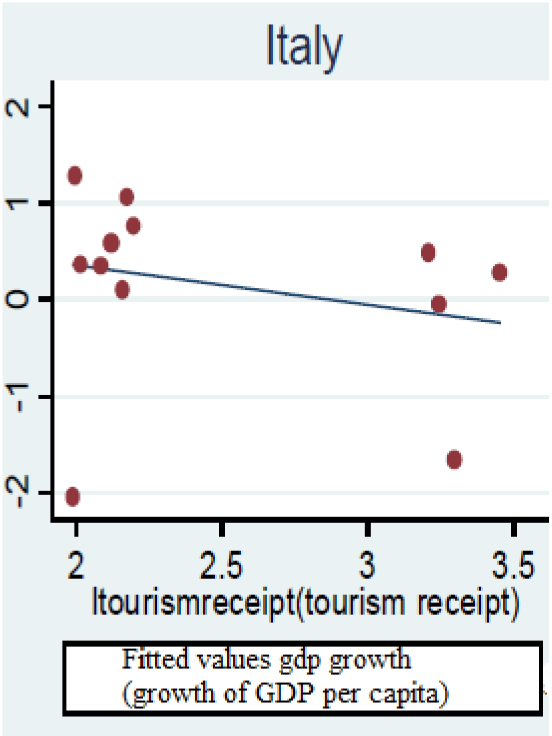

Figure 2 *Growth of GDP per capita (Italy)*

CONCLUSION

The paper shows that there are a variety of sources of funding available for tourism business or organization. When developing a funding proposal for tourism venture, we must ensure several points like understanding the funding source's criteria and understanding the advantages and disadvantages of the type of funding that you are considering (e.g. debt versus equity financing).

Tourism through the creation of attractions and provision of supporting infrastructure, can effectively create its own demand. For this aim, tourism has his own strategy. This strategy should provide a tourism management and marketing structure, supporting research and product development and giving attention to risk management in tourism business. From the above analysis, there is statistically significant proof of the relationship between the tourism receipts and economic growth. This relationship is positive and merely significant. Also the residuals of this regression when tested for stationarity, proved that they do not contain unit root, i.e. that the two series (economic growth and tourism receipts) are cointegrated. This is in line with the proof for causality. On the other hand, real effective exchange rate in presence of tourism receipts exerts negative and statistically significant relationship. While air departures as proxy for infrastructure exerts positive relationship with economics growth, exchange rate and tourism receipts. The implication is that international tourism expansion plays a relevant role for the economic growth in the economies mentioned above. The intense state intervention for tourism growth and especially for tourist economy, arises either directly from the performance of tourist infrastructure works or indirectly from the mechanism of funds and incentives. Generally, this is a characteristic feature of modern tourism, but also it is factual evidence that the state tries to develop tourism, which is regarded as one of the most important sectors of economic activity. All these countries are examples for economies that are moving faster with an important contribution of international tourism. In this way, governments should be aware of the potential positive role of tourism and thus how to gain a comparative advantage from such an economic activity.

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GREEN ENTREPRENEURSHIP AND SUSTAINABLE DEVELOPMENT OF TOURISM IN THE SOUTHEAST REGION OF THE REPUBLIC OF MACEDONIA

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Abstract

Green entrepreneurship is a special contemporary type of entrepreneurship that encompasses those activities of the company that in some way protect the environment and avoid pollution and damage. Green entrepreneurship entails carrying out business activities related to the environment and nature. Natural beauties, clean environment filled with lakes, mountains, waterfalls, thermal waters, ethno villages, monasteries, local manifestations, traditional food and hospitality are preconditions for the development of green entrepreneurship in the tourism sector in the South-East region of the Republic of Macedonia. In order to attract more tourists which will lead to the development of tourism in this region will be encouraged through the green entrepreneurship, it is necessary to apply an appropriate innovative approach in creating the offer and adjusting the activity of small businesses in the field of tourism.

Keywords: Green entrepreneurship, Innovation, Southeast region, Sustainable development

INTRODUCTION

Global changes in the environment force companies to be flexible, constantly looking for new concepts of work. Entrepreneurship is a process of innovation, financing and realization of business ideas, and the entrepreneur is a person who is the carrier of innovative activities, original ideas and possesses exceptional characteristics [1]. Companies operating in the tourism sector in the South-East region of the Republic of Macedonia are facing new challenges that are imposed from the new working conditions and the direction of the population towards the protection of the environment and exploitation of natural opportunities. Indeed, entrepreneurial firms improve both the static and the dynamic efficiency of the economic systems [2].

On the other hand, natural disasters - earthquakes, tsunami, extinction of many species of plants and animals, the occurrence of ozone holes, pronounced climate change, and so on, present a challenge for entrepreneurs to create innovative green businesses and respond to human behavior towards the environment. Among other positive contributions to the economy and the society, entrepreneurship has been mentioned as one of the most effective solution for solving many social and environmental concerns [3]. The increased number of affected people from various diseases, the extinction of certain plant and animal species, and the polluted environment (air, soil and water) represent real challenges for the entrepreneurs and confirm the need for the so-called "Green" businesses or green entrepreneurship.

Creating an original tourism offer in the field of green entrepreneurship is a perspective concept of the work that implies continuous environmental research, introducing an innovative concept by utilizing opportunities in the environment and innovation of entrepreneurs. The South-East region of the Republic of Macedonia is characterized with the potentials for development of green entrepreneurship in the tourism sector. Through the tourism and creation of an appropriate tourist offer, the development processes within the national economy are stimulated, the natural and cultural heritage is nurtured and it is contributed to the national integration of the people [4].

Geographical description and tourist potentials of the Southeast region

The Southeast region is one of the eight statistic and planning regions in the Republic of Macedonia. The region covers the Strumica-Radovish and Gevgelija-Valandovo valleys, i.e. the drainage area of the Strumica river and the lower catchment area of the river Vardar. According to the location, the region is a potential center for attracting domestic and foreign tourists. From an international point of view, the region is positioned between the Republic of Greece and the Republic of Bulgaria, on an area of 2,739 m^2 or 11% of the territory of the Republic of Macedonia.

The Southeast region extends to the southern part of the Republic of Macedonia. The geographical location of the region covers the above mentioned valleys and masses of the Belasica Mountains in the south, Ograzden to the east, Plachkovitsa to the north, Srta in the central part and the east side of Kozhuf Mountain. In the south it borders the Republic of Greece, the east with the Republic of Bulgaria, and to the north and west with the East and Vardar region. The region covers an area of 2,835 km^2, or 10.9% of the total area of the country. Natural beauties, clean environment, lakes, mountains, waterfalls, thermal waters, monasteries, local manifestations, healthy and traditional foods enriched with the hospitality of the inhabitants of the southeast attract the attention of tourists and passersby.

The tourist offer in this region consists of several aspects: thermo-mineral potentials, waterfalls, lakes (natural and artificial), historical sites and buildings, churches and monasteries, various types of events and manifestations, as well as certain tourist facilities. Companies that aim to offer an innovative tourist offer must face specific problems arising from the soil pollution, climate change and legislation. Green entrepreneurship is a process of successful management of sustainable development and corporate social responsibility. Green ventures represent a way through which entrepreneurship can fulfill the call for a greener and more environment-friendly business orientation, providing practical and innovative solutions to environmental problems [5].

Sustainable development of the environment is a simple concept, and a true understanding of the importance of sustainable development is risk management for a future that is influenced by natural phenomena and systems and social thinking. The integration of environmental practices in the tourism sector is a modern concept of work that creates the need for training entrepreneurs who will be able to take advantage of the opportunities of green entrepreneurship.

Green entrepreneurship and green jobs

Green entrepreneurship creates so-called "green" enterprises, that is, "green" businesses, whereby they can provide increased energy efficiency through utilization and saving of natural resources. In conditions of a pronounced degree of pollution and possible consequences due to inadequate behavior towards the nature and the environment, green entrepreneurship is a concept that provides sustainable development in the tourism sector.

All activities through which the planet is "greener", and measures taken to reduce pollution, encourage environmental business activities and the opening of innovative jobs in the tourism sector. The application of low carbon processes, technology without pollution, and recycling represent the potential for employment growth and increased economic activity of highly developed countries. The best green-oriented businesses use 3P technique - profit, people and the planet.

Green jobs originate from those activities in the tourism, agriculture, manufacturing, research and administrative sectors that contribute to the preservation or renewal of the quality of the environment. Among other things, green jobs include jobs that help protect ecosystems and biodiversity; reducing energy use, utilizing renewable energy sources, water consumption through highly efficient strategies and reducing or avoiding all types of waste and environmental pollution. Green enterprises or VC firms are, on average, more prone to invest in an emerging sector (such as the green sector), if the sector is legitimized. There are two mechanisms that determine emerging sectors' legitimacy: (positive) media attention and government support, which both hold for the green sector [6]. Achieving greater sustainability is provided through the transformation of the following activities: creating new jobs in production processes that pollute the environment, supplementing and installing equipment to reduce pollution, replacing some jobs with others, for example, in switching from the use of fossil fuels to renewable energy sources; from truck transport by rail, or by replacing landfilling and combustion of waste by recycling, additional qualification of certain workers for already existing jobs through short training, methods of work and profiling to carry out green work activities, creation of new positions through the education system, training and re-training organized by entrepreneurs, independent trainings and trainings for easier self-employment.

Green jobs involve a wide range of skills, educational background and professional profiles that are necessary for the development of the green economy. This is especially true for the so-called, indirect jobs, especially in those of the distribution industries. The new potential is the emerging industries, such as wind and solar energy, where the supply chain played a key role in the traditional industries. Technological and systemic opportunities offer different degrees of environmental benefits and different categories of green jobs. Greater efficiency in the use of energy, water and materials is the main goal.

Business ideas for green entrepreneurship in the Southeast region

Tourism has the power to influence and change the environment. Tourism must provide protection of the environment, protection of natural tourist resources and attractions, to meet the needs and motives of tourists, while ensuring its sustainability. The Tourism-Environment relations are not simple, on the contrary they are very complex. Their relationship evolved and changed over time, depending on the period and dynamics of the development of tourism. As an example of sustainable development and environmental protection in this paper, we present the Park of wind power plants "Bogdanci". In the future, it would be possible to make tours for visiting tourists on this windmill park.

Macedonia has a great wind potential, which is confirmed by measurements of several micro locations. Park of wind power plants "Bogdanci" (PVE "Bogdanci"), also known as the Windpark "Bogdanci" - a wind park near the town of Bogdanci, southeastern Macedonia. It construction began in May 2013 and was completed in just under a year, in February 2014.

The wind park "Bogdanci" is located beside the town of Bogdanci, on the hill Ranevec. PVE "Bogdanci" with 16 wind farms spread over 29 hectares is expected to deliver at least

100 gigawatt hours of naturally viable energy, which is annually enough to supply 60,000 households to households [7].

The first phase of the project ended with the complete upgrade and completion of all 16 windmills in February 2014, while in March 2014 the activities for their connection with the transmission network of MEPSO were underway. After the connection, a trial period was followed to examine their operation and to check the entire technical equipment, after which the capacity entered the regular production.

In the course of March 2014, the infrastructure and associated facilities of the wind park were completed, such as road infrastructure, connection of the new power line, command building and 20/110 kV substation.

In the second phase of the project, it is envisaged to complete it with six more windmills, with what the installed capacity of this energy will reach 50 megawatts, of which approximately 125 gigawatt hours of green energy can be received annually.

Recommendations and guidelines for the development of green entrepreneurship in the tourism sector in the South-East region

The Southeast region has the great opportunities and potential for development of green entrepreneurship, creating an original tourist offer and satisfying the various needs of visitors-tourists, as well as the population in this region. Green enterprises need to focus on tourism because there are real opportunities for growth and development in real terms due to the existence of suitable natural tourist facilities and opportunities for using renewable energy sources [8]. The development of tourism in this region depends on the provision of certain preconditions.

The basic prerequisite for encouraging the development of tourism through the concept of green entrepreneurship in this region is the existence of an entrepreneurial initiative and culture for exploiting the opportunities of natural sources of the energy for sustainable development, creating an appropriate tourist offer and various contents that are an integral part of the touristic offer. The concept of green entrepreneurship in tourism enables the utilization of the benefits of effective environmental management through cost reduction opportunities achieved through effective waste and energy recycling initiatives, the need for implementation of the ISO 14001 standard for the protection, preservation and improvement of the environment, as well as increasing the awareness of the citizens about the rational utilization of natural and limited resources.

Establishing and improving the work of green tourism companies imposes the implementation of original processes of organizing the work that are based on the real situation and possibilities for using renewable energy sources. On the basis of the potentials available to the South-East region, possible recommendations for encouraging the development of green entrepreneurship would be the following: creating an appropriate innovative offer in order to achieve a high level of synergy and correlation between environmental protection and the use of natural resources, an appropriate information and education system for entrepreneurs, training and education of human resources in this sector, application of ecological concepts in all segments of operation and use is the possible ways to financially support eco-activities.

CONCLUSION

Environmental protection is one of the biggest challenges in the operation of the enterprises. Promotion of sustainable ecological development and intelligent energy use are the most important goals. Encouraging the green economy through eco-innovations and environmental services contribute to the utilization of business opportunities in the tourism sector. Energy efficiency and energy savings are crucial for environmental protection and the most effective way to achieve an energy-sustaining future. Green enterprises and their potentials for constant innovation and utilization of renewable energy sources create an opportunity for an original appearance on the market and introduction of new original offer in the tourism sector on the territory of the Southeast region. The concept of green entrepreneurship in tourism enables the utilization of the benefits of effective environmental management through the cost reduction opportunities achieved through effective initiatives for waste and energy recycling, as well as the need to implement the ISO 14001 standard for the protection, preservation and promotion of the environment. Achieving greater sustainability is ensured through the transformation of the following activities: creating new jobs in production processes who pollute the environment, supplementing and installing equipment to reduce pollution, replacing some jobs with others, for example, in switching from the use of fossil fuels to renewable energy sources.

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IMPACT OF EXCESS AIR ON ENERGY EFFICIENCY OF INDUSTRIAL OPEN-FLAME FURNACES

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Abstract

Industrial production has been driven by the requirements of maintaining or improving product quality and minimization of production costs. Within this requirement the overall energy management plays important roles. It is a known fact that the improving fuel utilisation efficiency is the key to good financial and environmental practice. To meet the higher requirements it is necessary to improve existing furnace by optimising the energy efficiency and by reducing the pollutant production of burners and combustion chambers. Among other things, the efficiency of combustion in the open-flame furnaces is one of the key factors in minimization of energy consumption per unit of product. The impact of excess air on the energy efficiency of an open-flame furnace is analysed in this paper.

Keywords: Industrial furnaces, Open-flame, Combustion efficiency, Excess air

INTRODUCTION

In most industrial heating processes, fuel represents a considerable fraction of the total cost of manufacturing. The difference between fuel saving and fuel wasting often determines the difference between profit and loss. Side effects of fuel saving often include better product quality, improved safety, higher productivity and reduced pollution.

The words 'economy' and 'efficiency', when used in their true sense in connection with industrial furnaces, refer to the heating cost per unit weight of finished, sellable product. 'Heating cost' includes not only the fuel cost but also the costs of operating and superintending, amortizing, maintaining, and repairing the furnace, and the costs of rejected pieces. In many furnaces, fuel cost may be a major item of expense. Therefore, economy is worthy of constant watching for reasons discussed earlier and because of frequent vacillation of fuel prices and availability.

There are several different solutions for improving the furnace energy efficiency with optimization of the combustion process. One of the most effective ways is to introduce contemporary equipment for preheating the combustion air. Also, fuel savings may be achieved by the replacement of the existing conventional combustion technology by the so-called 'advanced' commercially available combustion techniques: High Temperature Air Combustion (HiTAC) and Oxy-Fuel combustion. Namely, high temperature air combustion of heating furnace is characterized by reactants of high-temperature and low-oxygen concentration. Many researchers have recently realized significant energy savings, NO_x emissions reduction and heat transfer uniformity in industrial heating furnaces resulting from such novel combustion [1-4]. Oxy-Fuel combustion or oxygen-enhanced combustion (OEC) can, on occasions, offer some of the following benefits: increased furnace production, reduction in specific fuel consumption, improved product quality, greater operating flexibility, improved refractory life and substantially reduced pollutant emissions. These benefits must be offset against the cost of oxygen and the capital costs of combustion equipment modifications and on-site installation of storage or production facilities. Thus, the economics of oxygen addition must be considered for each particular application. In principle, the proportion of oxygen can be increased up to 100% using the Flameless Oxy-Fuel burners, i.e. pure oxygen can be used instead of air. However, safety considerations dictate that very high level of oxygen is often limited to 25% if conventional burners are used [4,5].

In order to choose the optimal combustion technique, the cost–effectiveness analysis of individual offers may be carried out by comparing the following factors as indicators of the thermal efficiency of the system: combustion efficiency, available heat and fuel saving, taking into account the amount of harmful substances into the environment.

However, the above solutions are associated with substantial financial costs. For this reason, it is necessary to take into account the profitability of the investment i.e. the payback period.

On the other hand, there are significantly cheaper and also effective solutions. One of them is use a quality air/fuel ratio controller. The loss due to incomplete combustion of the fuel can be avoided by improving by fuel/air mixing and, oftener, by operating with some excess combustion air. It is important to operate at the lowest level of excess air as close as possible to stoichiometric ratio, i.e. practically no more than a very slight trace of CO should be present (Figure 1). The percentage of excess air depends mainly on the type of fuel and the burner design. In industrial practice, natural gas is being burnt with 5÷20%, and oil fuel with 15÷30% excess air [6].

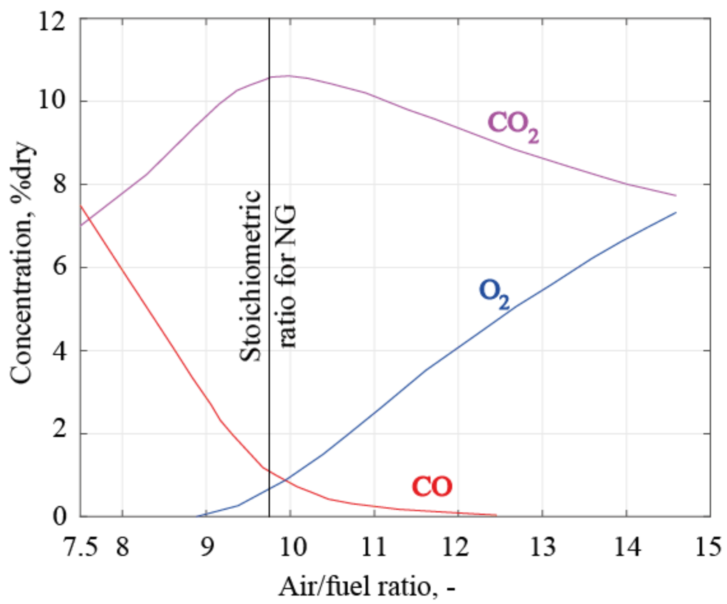

Figure 1 *Effects of air/fuel ratio on the composition of combustion products [6]*

Air/fuel ratio control is essential for:

- Efficient operation;
- Flame stability and safe operation;
- Control of emissions to avoidance of CO and un-burnt gas emissions;
- Product quality control.

However, in practice, care should be taken not to add more air than is necessary to complete the combustion process, since the addition of excess air has the following negative effects:

- The combustion efficiency is markedly reduced because of increased mass flow rate of flue gases leaving the furnace;
- The reduction in radiative heat transfer because extra air reduces the proportion of carbon dioxide and water vapor in the diluted combustion products;
- The rate of radiative heat transfer can be significantly reduced owing to the maximum flame temperature is not reached.

Calculations of the effect of excess air at combustion of natural gas

Calculations are based on combustion of natural gas of the following composition:

97% CH_4, 2.06% C_2H_6, 0.80% N_2, 0.14% CO_2. The net heat value $H_i = 34.18\ \mathrm{MJ/m_n^3}$.

a) Combustion efficiency

The energy efficiency of an open-flame furnace is generally defined as:

$$\mu_f = \frac{\text{energy transferred in a furnace}}{\text{energy input to the furnace from external sources}}, \qquad (1)$$

where the energy input supplied from external sources is usually the chemical energy of the fuel no taking into account the energy introduced with the fuel and/or air preheated by way of the exhaust gases.

The *combustion efficiency* (η_f) is defined as [3]:

$$\mu_f = \frac{h_{\text{fuel(NHV)}} + h_{\text{air}} + h_{\text{flue gas(inlet)}}}{h_{\text{fuel(NHV)}}} \qquad (2)$$

where $h_{\text{fuel(NHV)}}$ is the net heat value of the fuel, h_{air} is the enthalpy of the preheated combustion air, and $h_{\text{flue gas(inlet)}}$ is the enthalpy of the gas at the inlet of the recuperator.

As can be seen from the expression (1) the enthalpy, i.e. the mass flow rate of flue gases leaving the furnace has the greatest impact on reducing the combustion efficiency. Calculation results of the losses of energy are presented as relationship between the energy loss with flue gases in the furnace outlet and the percentage of excess air and temperature of flue gases (Figure 2). Energy loss with flue gases is displayed in percent of the net heat value.

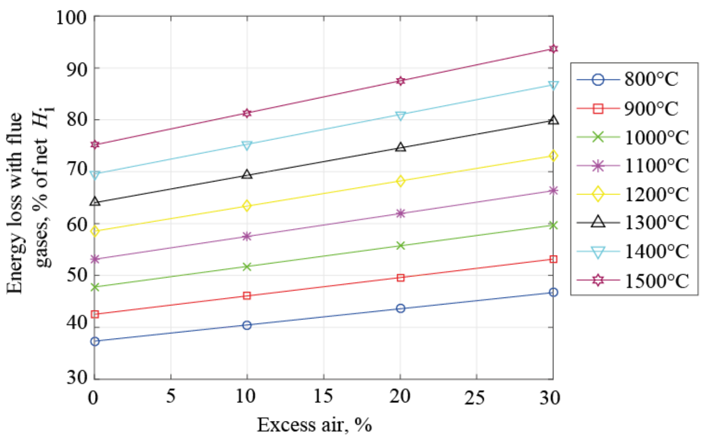

Figure 2 *Relationship between energy loss with output flue gases and excess air and temperature of flue gases*

b) Adiabatic flame temperature

For the calculation of adiabatic flame temperature was used the following relation:

$$\vartheta_{ad} = \frac{h_{cp}}{c_p} \tag{3}$$

where h_{cp} is the enthalpy of the combustion products and c_p is the average specific heat of the combustion products. To determine the adiabatic flame temperature, it was necessary to use the iterative procedure assuming the same. The calculation results of the adiabatic flame temperature for different values of excess air are shown in Figure 3.

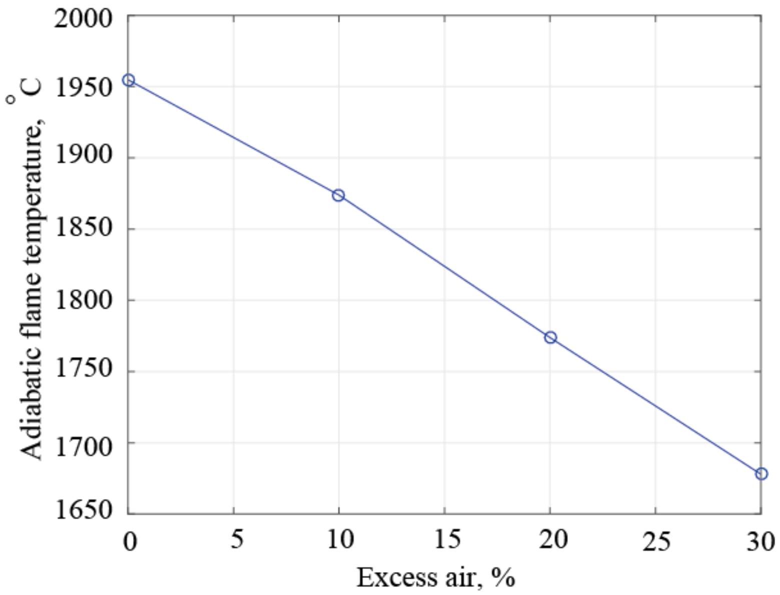

***Figure 3** Effect of excess air on the adiabatic flame temperature*

c) Composition and emissivity of combustion products containing CO_2 and H_2O

Calculations of the air requirement and composition of combustion products for combustion with stoichiometric air and with excess air were carried out using the standard equation for combustion of gaseous fuels [7]. The calculation results of the composition of combustion product are shown in Figure 4.

The emissivity of combustion products as a function of temperature of a gas body and a product term $p_i L$, where p_i is the partial pressure of gas i and L is the beam length were determined utilizing the charts from Hottel and Egbert [8]. The assumed value for the equivalent path length for radiation from a gas body is $L = 2$ m. The results of the emissivity of combustion products for different values of excess air are shown in Figure 5.

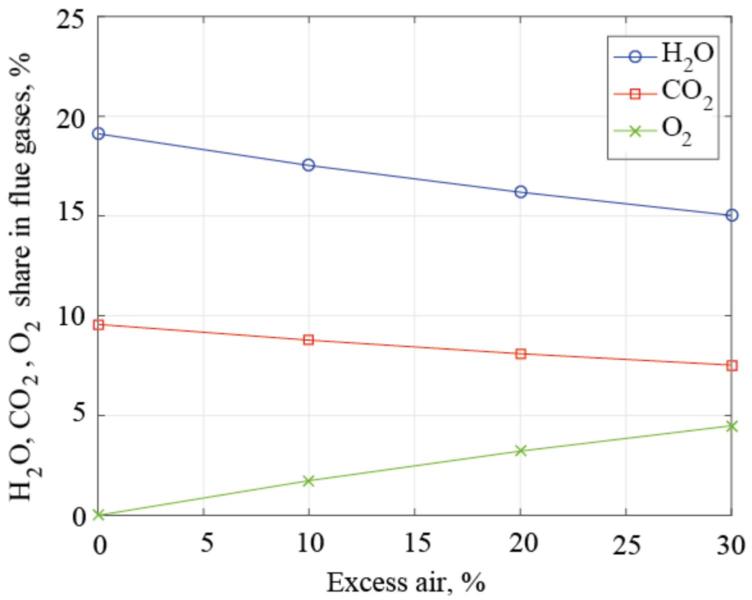

Figure 4 *Relationship between proportion by volume of CO_2, H_2O, O_2 in wet combustion products and excess air*

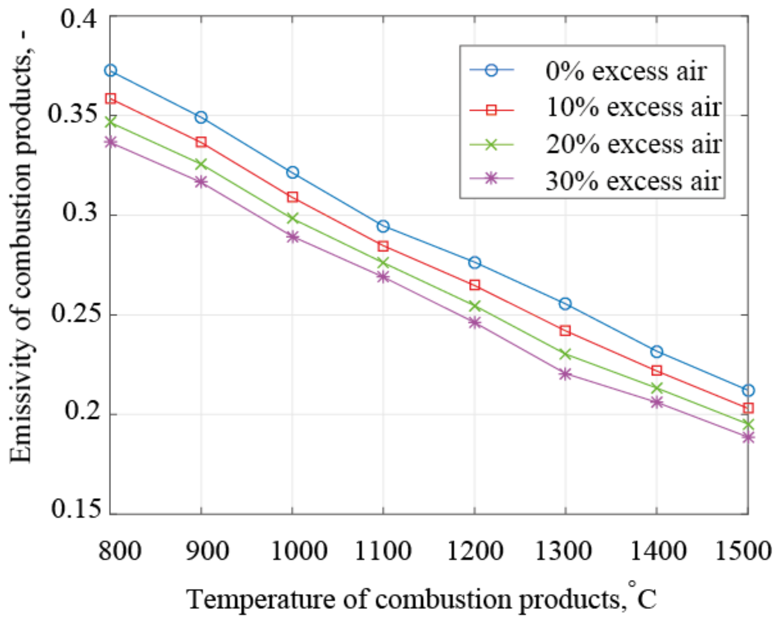

Figure 5 *Variation of emissivity of combustion products containing CO_2 and H_2O with excess air*

RESULTS AND DISCUSSION

If more air than is necessary for complete combustion is added, for example from 10 to 30%, the energy loss with flue gases living the furnace working space increases for 10% at 1300°C, or for 8% at 800°C temperature of flue gases (Figure 3). The change in excess air in the same range reduces the adiabatic flame temperature for 200°C (Figure 5). This, in turn, results in a marked drop in the rate of radiative heat transfer because radiation is proportional to T^4. Due to dilution by excess air, the proportions of CO_2 and H_2O in the combustion products are reduced for about 3% (Figure 4) decreasing the emissivity for 8% (Figure 5).

Based on the results it can be concluded that the reduction in flame temperature and the increase in energy loss with output flue gases are two main factors in reducing furnace energy efficiency while the reduced proportions of CO_2 and H_2O in the combustion products have a lesser impact. Just drop in flame temperature from 1600 to 1500°C can result in virtually a 20% in radiative heat transfer [6].

In open-flame metallurgical furnaces, the heated metal is in direct contact with combustion gases. Radiation heat transfer takes place in the system: combustion gases-metal, combustion gases-wall and wall-metal. The resulting heat flow is specific for each furnace as well as for the characteristics and temperatures of metals, combustion products and walls. For this reason, for each particular furnace, the influence of the factors described above on the resulting heat flow reduction should be analyzed as it is done in Lazić and Grubišić [9].

CONCLUSION

In practice, natural gas is often the default choice as a fuel in industrial furnaces, although because of its low carbon/hydrogen ratio results in low emissivity combustion products and relatively poor radiant heat transfer. There are many options for increasing the energy efficiency as well as improving performance of the industrial furnaces. To overmatch the challenges of rising energy cost and environmental regulations, the furnace user is necessary to choose the best possible options with respect to: performance, energy efficiency, low emissions and low maintenance, taking into consideration the investment costs. In this paper, the emphasis is on the importance of maintaining a proper fuel/air ratio in order to increase the energy efficiency of an open-flame furnace.

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TOWARDS DESIGN FOR SUSTAINABILITY: ECODESIGN - PAPANEK & MALDONADO

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Abstract

Ecodesign is a method to design with consideration for the environmental impacts of the product. In the post-second-world-war era and environmental pollution and high consumption, a faction of designs emerged that sought to redefine theory and practice and to politically and ideologically set against technical rationality. At the end of the sixties, a new terrain is emerging that will give design a completely new perspective. Till then, design has been preoccupied by the creation of a product, but it has not been interested in the whole life circle of objects. Today, this aspect of the design product represents one of the most important part of the design process. In the literature, this new field – eco-design – is a new field of political-ideological occupation of the design stand point. This paper will explore development of ecodesign in historical context with emphasis on theories of Papanek and Maldonado.

Keywords: Design, Sustainability, Ecodesign, Ecology, Environment

INTRODUCTION

Jean Baudrillard (1929-2007), with a critical review of the rise of semiotics in the field of design, offered a new design concept. Baudrillard, by combining different philosophical traditions, offered a critical analysis of the society based on postmarksism and linguistics. In book *The Twilight Symbol*, Baudrillard recognized new ideological-political directions and activities of design practice and enabled the recognition of the problems that the design was occupied from the end of the sixties and the beginning of the seventies of the twentieth century. Starting from the thesis that *the object is a subject for another subject* [1], Baudrillard defines the problem of the world without any manufacturers or consumers on the one hand, it is a matter of two subjects that are symbolically exchanged through one subject.

Baudrillard thinks that the new methodology of design practice, which includes scientific and semiotic disciplines, has entered a new phase of conducting expanding consumption through a system of traffic values that enters into all domains of social life. From the body, sexuality, information, culture, everyday objects, space, even those elements that up to then touched upon the political economy, everything has now fallen under the influence of traffic values. Baudrillard maintains that society is found in the world of codes in which all signs are exchanged, and that they do not correspond to the actual use value. They circulate, communicate, broadcast, without knowing who or why.

Baudrillard thinks that the design, since its beginning, has set itself the social and political goal of promoting the greater transparency of social relations through democratization of the environment, democratizing society and making everyone equal to the subject. Design, on the one hand, has become a servant of economic policies, but has retained some of its initial ideology. In this sense, we see two design policies, one that *surrendered*, and the other that avoid everyday design practice. In such a line of things, Baudrillard sees design as a victim of the two-way market system and fashion, since design cannot be expected to change the policy laws of the economy. However, he points out that designers are responsible because they can choose a production method. At the core is the political choice.

HISTORICAL CONTEXT

Given that the United States has become a reference to civilization, there has became new spiritual climate that will effect designers. During the 1960s, in American and European societies, deep social quakes were emerging, pointing to large scars in the system itself. The Movement for Civil Rights, bloody clashes, the War in Vietnam and Indochina, the 68th Revolution, the unrest and protest at universities, were just a reflection of the public awareness of the absurdity of the state in which the Western world was found. The processes of re-examining the economic and social goals, the patterns of behavior of corporate systems have begun, which, through their actions, has successfully flung such tendencies into the heads of individuals. Chaos and the dispersion of the order, as far as design is concerned, found its way in *the ecological movement* in the late sixties.

Victor Margolin (1941) in book *The The Politics of The Artificial* draws a writes texts that explain the transformation in design as a response to the world situation that has found itself in its own turmoil. The book states that designers had to depart from the design dogma that was bent on modernity and that it would continue to be concerned by exploring the role of design in sustainable development and integrating human beings into a wider ecological and cultural environment [2]. In this sense, Margolin calls on the studies of the Roman Club (a survey published under *The First Global Revolution: A Report by the Council of the Club of Rome* [3]). The Club of Rome, founded in 1968, is the initiative of Italian industrialist Aurel Pecei. The goal of the club was to investigate the complexity of the problem that is affecting people of all nations: poverty in the middle of wealth, environmental degradation, loss of government in institutions, uncontrolled urban expansion, employment problem, alienation, rejection of traditional values, inflation and other economic disturbances. The Club's main premise was to view the world as a unique system and analyze it as a whole.

The situation in which the world finds itself in the post-industrial era illustrates the division into two realities, and, as Margolin calls it, the first *sustainable model* and the other *expansionary*. The assumption of the first model is the worldwide system of environmental countermeasures that make consumable resources. The first model received broader support as the ideal to be sought for, it has fostered the establishment of a large number of green social and political organizations. Contrary to this model, there is another expansive model, according to which the world consists of markets in which products function as symbols of economic exchange. The main factors of this world are capital, investment, production, private and corporate wealth, the global market mainly oriented to the developed economic systems of North America, Europe and Japan. Margolin recognizes the collision of these two models and trunks that remain in the vacuum of non-institutional communication, and is committed to finding a compromise, the optimum solution that these two models will reconcile and provide the sustainable development of the planet in general. Margolin believes that it is necessary to find a solution in new forms of democratic public spirit. It is necessary to restructure the whole world economy, which would essentially mean a change in the assumption that governs in advanced economies, whereby a comfortable life and a high standard of living are available to everyone. The cost of cleaning contaminated runes and air, if balanced ecological planes are to be balanced, is extremely large.

When the design ideology of theory and practice is concerned, Margolin thinks that design must move away from the dogma it has been subjected to so far and that it should be embedded in researching the role of designers in the sustainable development and integration of human beings into a wider ecological and cultural environment. Margolin saw design as the place of the union and the reconciliation of two models, if the design re-imagines and redefines it as a discipline of comprehensive conceptualization and environmental planning [2]. Thus, design is the power that creates plans, projects, products and has tangible results. A good design has the discreet skills of observing, analyzing, inventing, shaping or giving forms of communication.

FIRST ECODESIGNERS

In design practice two very important figures have emerged as advocates of a ecodesign. In the United States the revolutionary advocate was Viktor Papanek, and in Europe was Tomas Maldonado.

Papanek's book *Design for the Real World*, from 1971, marks a milestone in designing mass production, particularly in Severn America [4]. *Design for the Real World* is a genuine sociological and cultural study of industrial design and its roles in the period of great historical chaos. Papanek has started from a revolutionary standpoint that *a few profession is more damaging than industrial design, and only one - propaganda design – is crooked and sloppy* [4].

Design is crooked in the sense that it represents means of capital, an unfair profession that persuade people to buy things that they do not need, with money they do not have. In this context Papanek demystifies the social role of the design profession. In a society that consumes excessively, lives in a society of abundance, with motives and goals managed and manipulated by large capital - the designer does not work for those who need it but for those who have it. With such attitudes and concrete examples, Papanek actually points out the moral and political-ideological crisis of the design profession at the beginning of the seventies of the twentieth century.

Figure 1 *Viktor Papanek (1927-2007)*

In fact, Papanek opens a page of a new look at the world and the living environment in which he conceives the concept and ideology of design. He believes that the lacrudge ideology brought by the consumerism is just a lie of a civilization, the more important the interest of the fetishization of technological aesthetics than the real problems of modern society dominated by capitalist-market relations. Such a design is used in a series of artificial obsolete tricks that are being manipulated by consumers on the market. In other words, consumers rather than consuming designed products, they have been consumed by it.

There are groups of young people, students, old people, handicapped people, babies, riches and others who are not seen as potential consumers of consumerism. Papanek's solution is shaped for the majority rather than the minority. Shaped for the people of the Third World, which shows their own example.

Namely, Papanek spent a long time in Scandinavian countries, Peloponnese, Eskimos, Hopi and Navaho Indians, worked as a UNESCO expert, worked in different parts of the world, and developed his design for human needs. He designed for the poor, for people from underdeveloped countries with more modest income. With this kind of comprehensive design, Papanek has really wanted to show that the designer has to re-confirm position in society again. Instead of shaping it in perfect peace and capital dignity, design has to turn to society and be socially engaged.

Design as a special technical practice in the industrial development of Europe in the sixties and seventies emerged from the thinkers who emerged on the historical dimension of the environmental problem. Among them, Tomas Maldonado explained that:

(...) the human environment is shaped by forces that exclude our control and our influence. We were found in the ambiguous situation whereby we have nominally adopted the responsibility towards a society that in fact deals with others. The decisions are brought by others without us; often against us [5].

Maldonado actually points to the problems that arise during that period and offers a new European vision of a comprehensive design based on clear ideological and political grounds within the institution of society. Criticizing the affirmation of social status that glorifies the dominant class of the use of objects, he really wants to emphasize the design activities that are actually directed at the goals that act as a man's refinement.

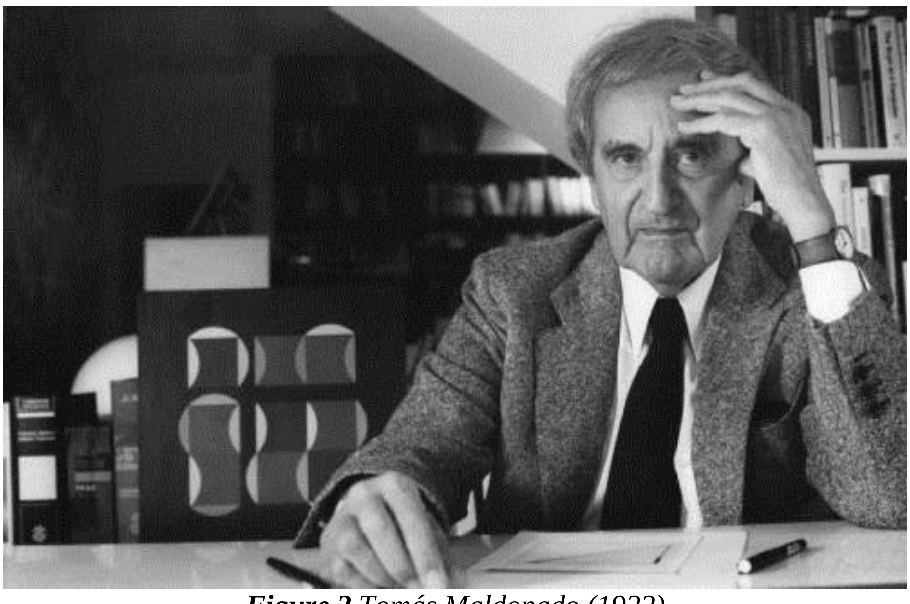

Figure 2 *Tomás Maldonado (1922)*

Maldonado recognizes forces that obstruct design work in the context of sustainable environmental ecodesign. He sees these forces as those groups of powers that have always acted solely to meet their own interests absolutely unskilled for the needs of the people. He thinks that the crisis of profession occurs through the blurring of the problems before the disappointment before which the profession is found. In design, the quest for the function idea yielded the opposite of what was expected, creating a product of sterile and refined formalism [5].

Maldonado criticizes outdated institutions working on old doctrines and do not offer the means for more radical changes in practice, primarily by reference to educational institutions. The school should function as an open sustainable ecosystem, transparent and adaptable, a new design concept that is able to respond to the complex problems of the world that was found in the period of great changes and environmental problems.

CONCLUSION

At the end of the sixties and seventies, the ideological crisis and the shadow of the design profession were divided into two parts, which are at the level of the divide on two models: the model of sustainable development (ecodesign) and the expansion model. Accordingly, the design was found in an ideological breakthrough on consumer design and a comprehensive design. Along the clash between the two models of the world, there are clear political-ideological settings seeking a place in society of power and control. The eighties and the nineties will latter on show that tensions between these two directions are not based on stylistic patterns but on political conscience or misguided attitudes and more openly show constitution of one field of design discipline – ecodesign.

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