FACULTY OF NATURAL AND TECHNICAL SCIENCES, GEOLOGY DEPARTMENT,
UNIVERSITY OF LJUBLJANA, SLOVENIA AND SLOVENIAN UNESCO-IGCP
COMMITTEE WITH A SPONSORSHIP FROM THE UNESCO ORGANIZE

3rd INTERNATIONAL WORKSHOP ON THE PROJECT

ANTHROPOGENIC EFFECTS ON THE HUMAN ENVIRONMENT IN THE NEOGENE BASINS IN THE SE EUROPE

PROCEEDINGS

Edited by:
T. Dolenec & T. Serafimovski
Ljubljana, 1-3 December 2011

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Language: English for presentations and papers

Aknowledgement:

This Workshop was organized with a financial support from the UNESCO-IGCP Participation Programme 2010-2011through the National Commission for UNESCO in Skopje, Republic of Macedonia

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GEOGENIC RADON POTENTIAL IN SLOVENIA

Asta Gregorič[1], Janja Vaupotič[1], Mateja Smerajec[1], Petra Žvab Rožič[2],
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Abstract

At sixty points uniformly distributed over the entire Slovenia, radon concentration was measured in soil gas, by exposing solid state nuclear track detectors in boreholes at depth of 80 cm. The average concentration of 36 kBq m^{-3} was obtained, with the highest values over carbonates. Thus, over carbonates radon geogenic potential was additionally studied in a smaller regular grid.

Introduction

The ^{222}Rn radon isotope (hereafter referred to as radon) originates from α-radioactive transformation of ^{226}Ra in the ^{238}U natural decay chain in the earth crust. Only a fraction (defined by the emanation coefficient) of radon atoms leave the mineral grain and migrate through the medium either by diffusion or advection and eventually enter the buildings or exhale into the outdoor atmosphere (Etiope and Martinelli, 2002). The level of radon activity concentration in soil gas is controlled by radon emanation and migration. It may be higher in the proximity of tectonic faults because of an enhanced exhalation of radon together with other gases due to the structure characteristics.

In the national survey in Slovenia, radon in air was measured in 1000 randomly selected dwellings (Humar et al., 1992), all kindergartens (730) and schools (890), a number of karst caves (with emphasis on the Postojna Cave), 5 major spas, 10 major water supply plants, 26 major hospitals, 8 major wineries and some others (Vaupotič, 2010). In more than 50 buildings, radon problem has been successfully mitigated. In recent years, our survey has been extended also to outdoor air (Vaupotič et al., 2010) and soil gas. In this work, radon was measured in soil gas at sixty points all over the country and in a regular grid of 13 points over carbonates (Lekočević, 2011). Radon levels are reported and discussed based on the geologic and tectonic characteristics of the area.

Geology of Slovenia

The most important geologic characteristics influencing geogenic radon concentration are the lithology and the presence of faults. For this purpose, our measurement points were grouped into 7 lithological units: clay-gravel deposits, carbonates, clastic sediments, sea and lake sediments, gravel deposits, Tertiary sediments and metamorphic rocks (Fig. 1).

Slovenia lies on the junction region between Alps and Dinarides which incorporates Eastern Alps, Southern Alps, Dinarides, Panonian basin and Adriatic – Apulia foreland. The Adriatic – Apulian foreland comprises south-western corner of Slovenia consisting of rocks of the Adriatic-Dinaric Mesozoic carbonate platform, and the flysch rocks resulting from its degradation. The entire southern part of Slovenia belongs to the Dinarides. Characteristic for them is the thrust and nappe structure, consisting mainly of carbonate rocks and sediments resulting from disintegration of the Adriatic-Dinaric carbonate platform: Upper Cretaceous carbonate turbidites, Cretaceous-Paleocene and Eocene flysch. The Southern Alps extend over the northern and north-western part of Slovenia. Mesozoic rocks of the Slovenian basin and Upper Triassic rocks of the Julian carbonate platform are exposed within them. The Eastern Alps are a geologic-orographic term comprising the complex of Precambrian and Old Paleozoic high and low grade metamorphic rocks, and of Permian and Mesozoic sedimentary rocks.

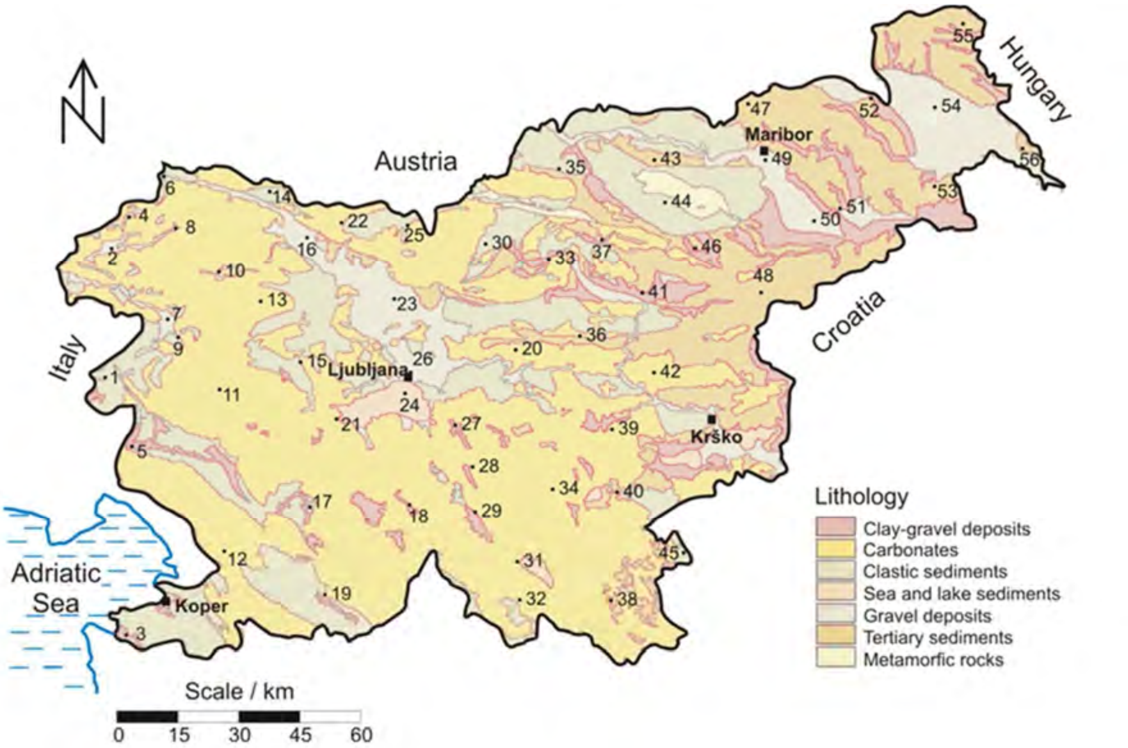

Fig. 1. Simplified lithologic map of Slovenia with measurement points.

The Pannonian basin, in the north-eastern part of Slovenia, consists of individual depressions filled with Paleogene and Neogene sediments of the Paratethys (marked as Tertiary sediments in the Fig. 1) (Placer, 2008). In addition to the major lithological units described above, also glacial and fluvio-glacial deposits, extending along major valleys, have to be considered (gravel and clay-gravel deposits). In the Ljubljana basin, situated in the central part of Slovenia, and in the Krško basin in south-east, the sea and lake sediments prevail.

Experimental

Measurement points for entire Slovenia, which coincide with the points of the national network of the permanent monitoring of gamma dose rate with thermoluminescent dosimeters located near meteorological stations, are indicated in Fig. 1. Except for the mountainous areas, the points were almost uniformly distributed over the country (surface area 20 thousand km^2) in an irregular grid with mostly 20 km × 20 km squares.

Time-averaged radon concentrations in soil gas were obtained by exposing the Radonlab solid state nuclear track detectors, based on a CR-39 foil, manufactured and provided by the Radonlab Ltd. Laboratories, Norway (Fig. 2a). After exposure, detectors were mailed to Radonlab for development and data evaluation. Detectors were calibrated by the manufacturer and in the IFJ-KR-600 Radon Chamber of the Laboratory of Radiometric Expertise, the Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland.

A borehole of 7 cm diameter was hand-drilled to a depth of 80 cm (Fig. 2b). A hard paper tube of 1 mm thick wall was inserted in order to prevent the hole from being collapsed (Fig. 2b). Then, a pair of detectors were hung one above the other, the lowest 2–3 cm above the bottom (Fig. 2a). The tube was closed on top by a plastic cover and with a layer of 5–10 cm of soil above it, and kept closed until the detectors were collected after 4–7 days. Because of logistic limitations, measurements were not carried out in a single campaign, but in August of 2006 and August 2007, always during a long period of hot and dry weather.

a)

b)

Fig. 2. *a)* Schematic view to solid state nuclear track detectors exposure in soil gas, *b)* Drilling of borehole and exposure of solid state nuclear track detectors..

An additional geogenic radon mapping over carbonates, covered by thick layer of eutric cambisol, was performed at 13 points in a regular grid of 10 m × 10 m. Points 1 to 4 are on the distance of 1 m from the main point 0, points 5 to 8 on 5 m and points 9 to 12 on 10 m, respectively (Fig. 3).

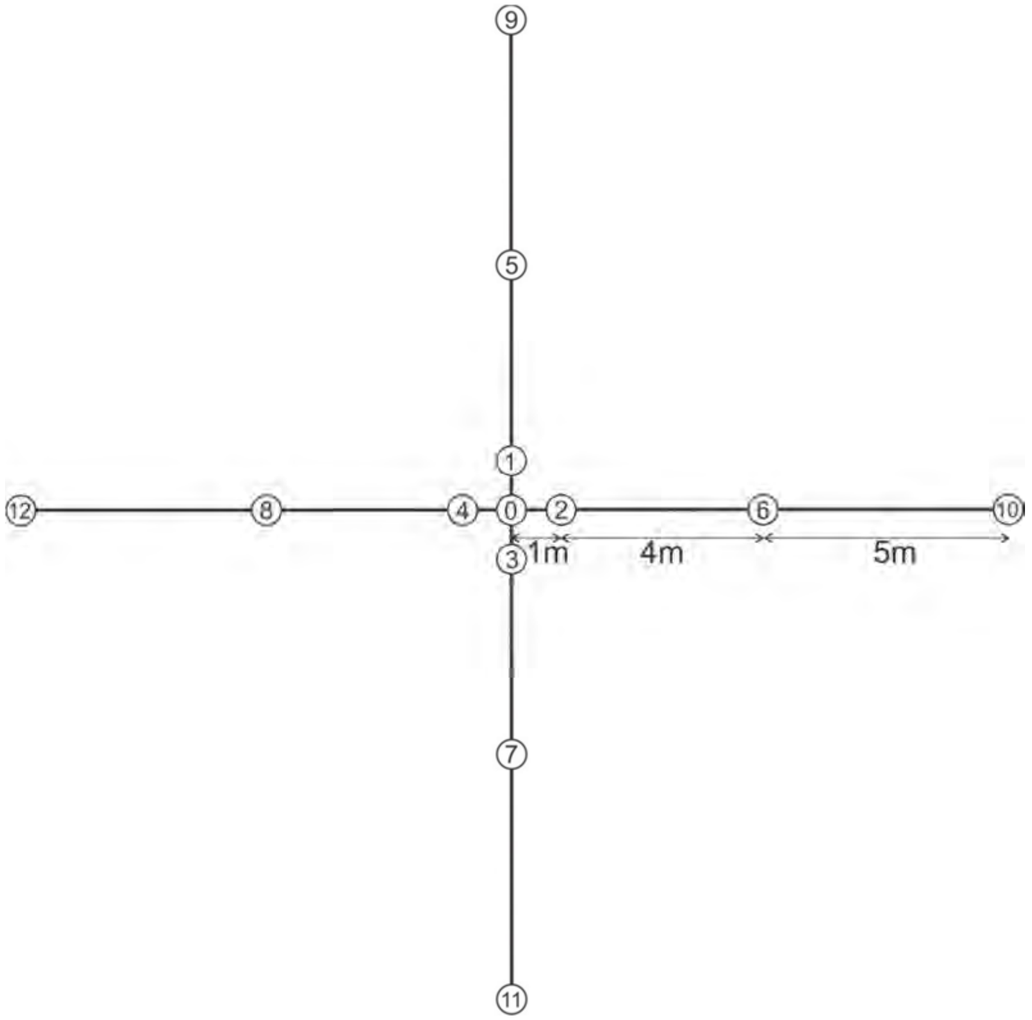

Fig. 3. Regular grid with 13 measuring points over carbonates.

Soil gas was sampled using technique adopted from Neznals'. A steel tube with a free sharp tip at the bottom end was inserted into the soil to depths of 50 cm and 80 cm. The tip was released and pushed for about 2 cm out of the tube into the soil, and soil gas was sucked into a scintillation cell (Fig 4a). After three hours, when radon reached equilibrium with its short lived decay products, gross activity concentration of scintillation cell was measured. The cells were manufactured at the University of Cantabria, Santander, Spain (Quindos-Poncela et al., 2003) and tested and calibrated by the Radon Center of the Department of Environment Sciences at the Jožef Stefan Institute and in the IFJ-KR-600 Radon Chamber of the Laboratory of Radiometric Expertise, the Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland. For activity measurements, a PRM-145 portable radon monitor (AMES, Slovenia) was used (Fig. 4b).

a) *b)*

Fig. 4. *a)* Soil gas sampling into scintillation cell, *b)* Alpha scintillation cell with PRM-145 radon monitor.

The cells are 0.31 dm^3 plexi glass cylinders, inside covered by silver-activated zinc sulphide foil. The bottom plexi glass window serves as optical contact to the end-window photomultiplier tube in the PRM-145 device. In order to comply with the quality assurance and quality control requirements, all measuring devices have been calibrated regularly both in our laboratory and in the IFJ-KR-600 Radon Chamber of the Laboratory of Radiometric Expertise, the Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland.

Results and discussion

Radon concentrations obtained in soil gas (C_{Rn}) at 60 points in the entire Slovenia are presented as box & whisker plots in Fig. 5. The overall ranges and arithmetic means are 3–211 kBq m^{-3} and 36 kBq m^{-3}, respectively.

The highest radon concentrations (Fig. 5), with an average of 50 kBq m^{-3} were found on carbonate rocks. In spite of low porosity of carbonate rocks, permeability is high because of the structural properties. Chemical solubility of carbonates results in karst phenomena, such as underground cavities, channels and corridors, which are possible pathways for radon transport. The lowest values were found over clastic sediments (9 kBq m^{-3}), sea and lake sediments (14 kBq m^{-3}) and on metamorphic rocks (10 kBq m^{-3}), all of them characterised by low permeability. At the points located on carbonates, clay-gravel deposits, gravel deposits and Tertiary sediments, 75 % of values ranged from several kBq m^{-3} to 75 kBq m^{-3}. The enhanced permeability of fractured rocks in the fault zones represents potential pathways for radon migration (Guerra and Lombardi, 2001; King et al., 1996; Seminsky and Bobrov, 2009). This is the reason for elevated radon activities at points 18 and 29 located on carbonates, points 9 and 37 on gravel deposits, and at point 46 on Tertiary sediments.

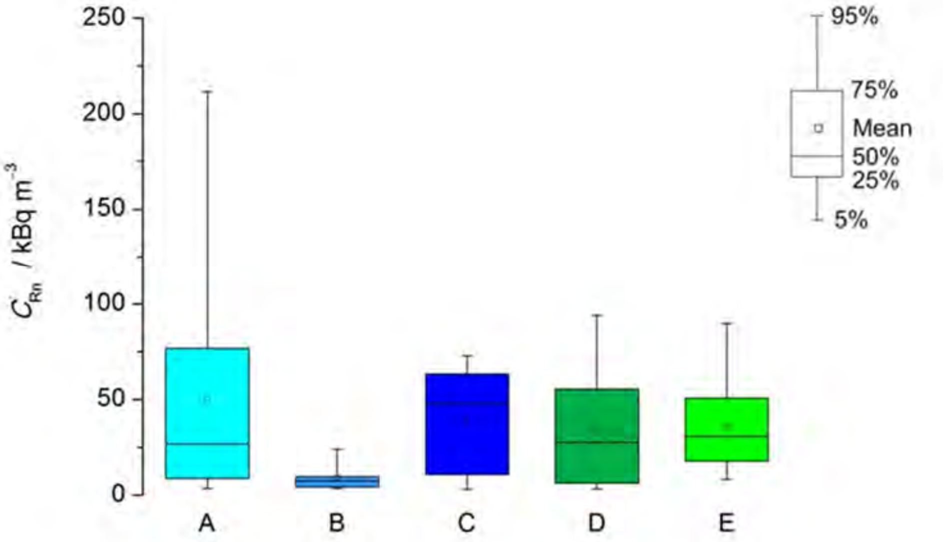

Fig. 5. Box & whisker plot of radon concentration in soil gas on different lithological units: **A** – carbonates, **B** – clastic sediments, **C** – clay-gravel deposits, **D** – gravel deposits and **E** – Tertiary sediments.

The geogenic radon potential map with indicated fault zones is presented in Fig. 6. Green casts present areas of normal (up to 10 kBq m^{-3}) values, and from yellow to red, of medium and elevated values. Elevated radon concentrations were observed in south and southwest of Slovenia (carbonates).

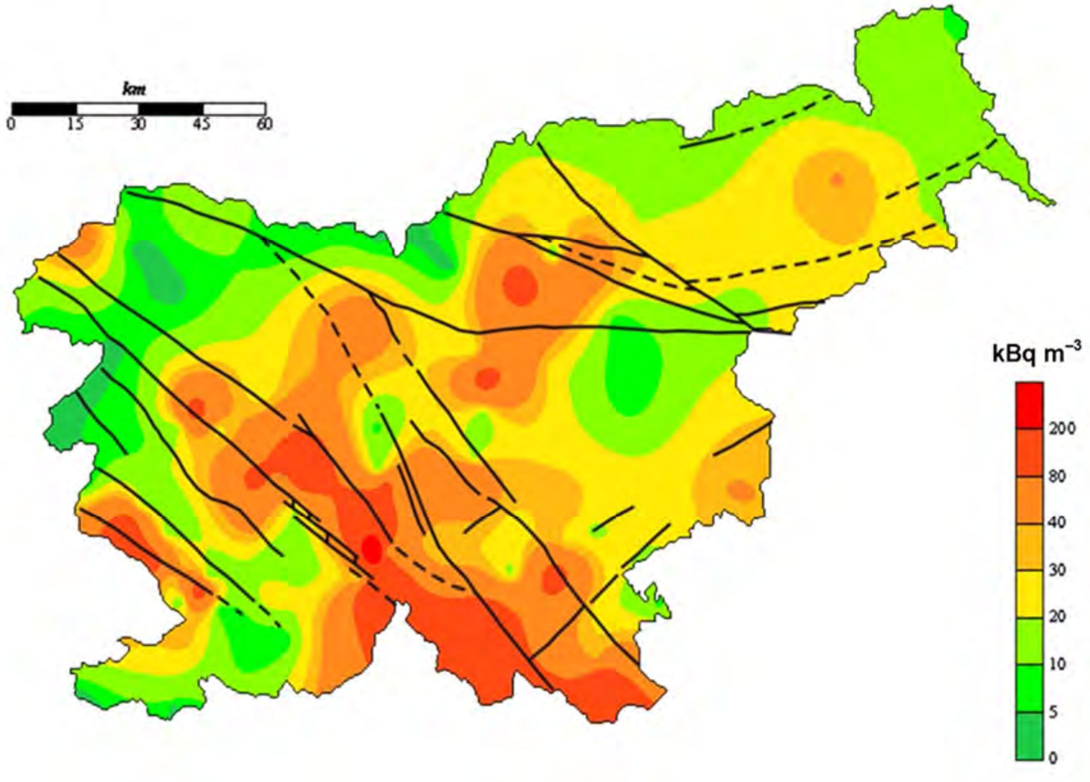

Fig. 6. Geogenic radon potential in Slovenia.

Results of two radon measurements in soil gas in a regular grid over carbonates are presented in Fig 7.

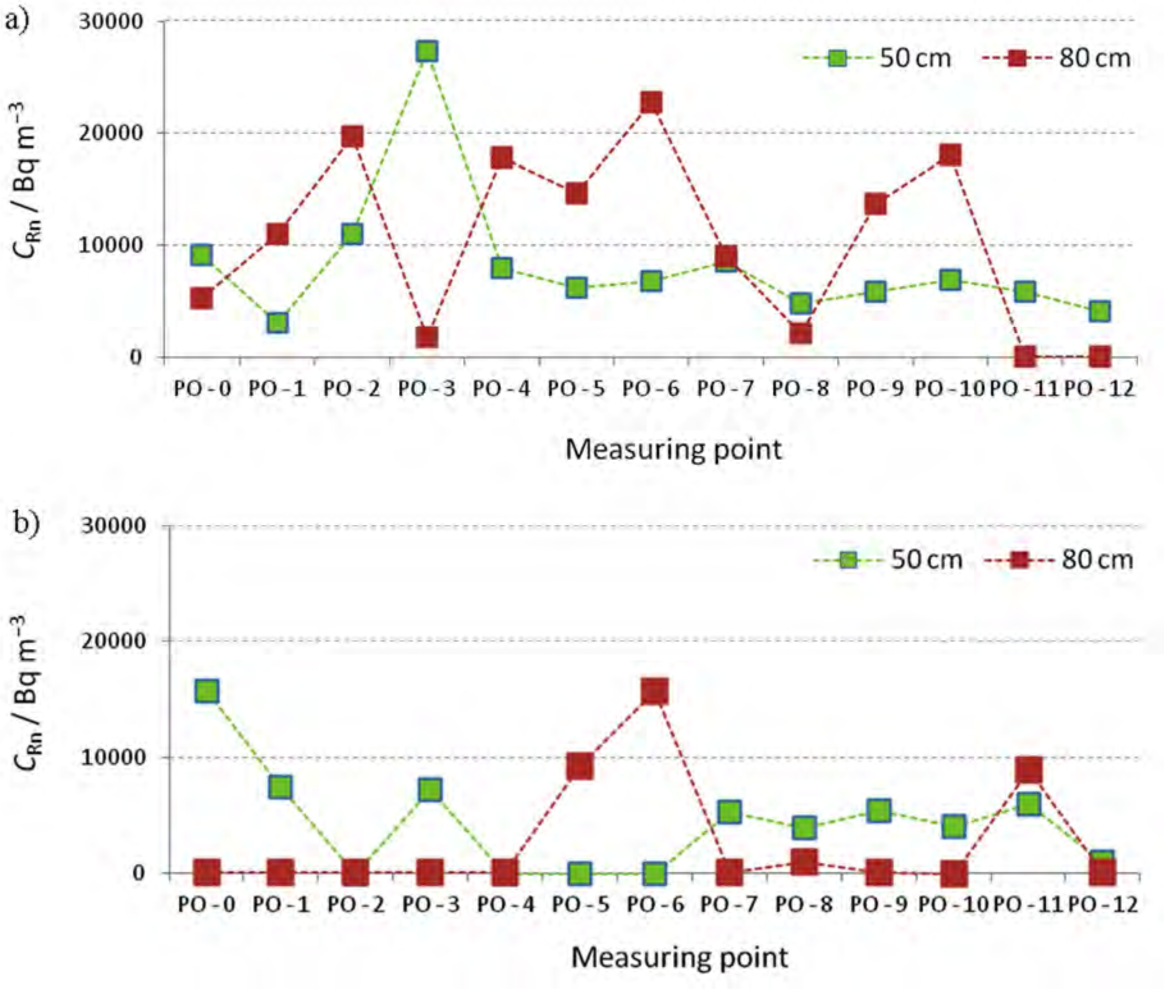

Fig. 7. Geogenic radon potential in a regular grid over carbonates on the depth of 50 cm and 80 cm.

The plot in Fig. 7a shows radon fluctuations within 13 measurement points at depths of 50 cm and 80 cm on July 7, 2011. As expected, higher concentrations, with a few exceptions, have been found at 80 cm, where soil was less permeable and thus the sucking of the soil gas into scintillation cell was reduced. On July 8, 2011, the field was covered by semi dry grass, cut the day before, immediately after soil gas sampling. As seen in Fig. 7b, the results were different, with radon flux from 80 cm completely blocked, except at points PO–5, PO–6 and PO–11. Obviously, the grass lying on the field increased the soil moisture. Due to the strong sun in the next day, the soil up to 50 cm was dried enough to enable satisfactory soil gas sampling (although radon concentrations were lower), but this was not the case at 80 cm.

Conclusion

Geogenic radon mapping at sixty points, uniformly distributed all over the county, have shown the range of radon activity concentration in soil gas of 3–211 kBq m^{-3} and arithmetic mean 36 kBq m^{-3}. With respect to geology, the highest values have been observed over carbonates in western and southern part of the country, with the arithmetic mean of 50 kBq m^{-3}. Elevated values have been also found at points in close proximity to the tectonic faults. The lowest values were measured over clastic sediments.

An additional study, performed in a regular grid over carbonates at depths of 50 cm and 80 cm, has shown significant fluctuations between the measuring points at both depths, and also an important role of unexpected changes of microclimatic parameters, as mowing grass in our case.

References

Etiope, G., Martinelli, G., 2002. Migration of carrier and trace gases in the geosphere: an overview. Physics of the Earth and Planetary Interiors 129, 185–204.

Guerra, M., Lombardi, S., 2001. Soil-gas method for tracing neotectonic faults in clay basins: the Pisticci field (Southern Italy). Tectonophysics 339, 511–522.

Humar, M., Šutej, T., Skvarč, J., Mljač, L., Radež, M., Ilić, R., 1992. Indoor and outdoor radon survey in Slovenia by etched track detectors. Radiation Protection Dosimetry 45, 549–552.

King, C.Y., King, B.S., Evans, W.C., Zhang, W., 1996. Spatial radon anomalies on active faults in California. Applied Geochemistry 11, 497–510.

Lekočevič, N., 2011. Spatial variations of geogenic radon within regular grids over carbonates and clastic sediments. BSc Thesis, Nova Gorica, p. 55.

Placer, L., 2008. Principles of the tectonic subdivision of Slovenia. Geologija 51, 205–217.

Quindos-Poncela, L.S., Fernandez, P.L., Sainz, C., Arteche, J., Arozamena, J.G., George, A.C., 2003. An improved scintillation cell for radon measurement. Nuclear Instruments & Methods in Physics Research 512, 606–609.

Seminsky, K.Z., Bobrov, A.A., 2009. Comparative assessment of radon activity for different fault types and scale ranks in the Baikal Rift and South of the Siberian platform. Doklady Earth Sciences 427, 915–919.

Vaupotič, J., 2011. Slovenian approach in managing exposure to radon at workplace. Nukleonika 55, 565–571.

Vaupotič, J., Kobal, I., Križman, M., 2011. Background outdoor radon levels in Slovenia. Nukleonika 55, 579–582.

MOBILITY OF METALS IN SASA MINE TAILINGS DAM MATERIAL

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Abstract: This study aimed at evaluating the fractionation of metals in tailings of Sasa Zn and Pb mine. Two sequential procedures (modified BCR and Tessier's scheme) were used to evaluate the extraction selectivity of different extractants. Systematic variations in particular fractions shows that the fractions are only empirically (operationally) defined and are not totally exclusive to the specific mineral phase. By far the most mobile metal in Sasa mine tailing is Pb that acid soluble fraction represent 50 % (BCR) and 60 % of total metal concentration (Tessier's scheme), respectively. The Pb association with different fractions decrease in the order: B1 > B4 ~ B3 ~ B2 (BCR scheme) and T2 > T3 > T5 > T4 > T1 (Tessier's scheme). High mobility potential was also observed at Cd that showed the highest association with oxidizable fraction (67 % in BCR scheme and 33 % in Tessier's scheme). Results shown that due to high mobility of metals, tailings from Sasa mine represent a serious threat to the surrounding environment.

Introduction

Metal mining, smelting, and processing introduce metal contaminants into the environment through gaseous and particulate emissions, waste liquids and solid wastes. The methods used to investigate the solubility and mobility of metals from mining and smelter-contaminated soils include measuring the distribution of metal contaminants with progressive depth in soil profiles, monitoring the mineralogical properties of contaminants to determine potential for dissolution and transport, the use of chemical partitioning methods to indicate soil chemical constituents responsible for sorption and release of metals, and the use of leaching experiments and water monitoring in the environment to determine the impact of specific contamination regimes (McGowen and Basta, 2001). Many mine and smelter sites contain amorphous waste materials that are very difficult or impossible to characterize using direct mineralogical methods (XRD, SEM-EDX). Indirect mineralogical methods or other techniques are used to investigate the release and potential transport of metals from such materials. Indirect methods are qualitative predictions based on solution species activities and do not provide the explicit evidence of definite mineral identification.

Tailings are mixture of waste ground rock, spent processing water and reagents produced at mine processing plant through ore extraction and manufacturing. The properties of tailings are dependent on the ore body being mined, the grinding and processing circuits, the reagent properties and the thickening process prior to disposal. The chemical and physical properties and the prevailing environmental conditions affect the rate of weathering of tailings and therefore the rate of metal release.

A variety of leaching techniques are used to simulate different environmental conditions. Sequential extractions estimate the amount of potentially toxic elements in various solid pools or "reservoirs" where the solid sample is subjected to successive attacks with a series of progressively harsher reagents to dissolve increasingly refractory forms (Tessier et al., 1979; Tessier and Campbell, 1988; Ruby et al., 1996; Quevauviller et al., 1997; Sahuquillo et al., 1999; Dermatas et al., 2006; Anju and Banerjee, 2010). They were first designed for the selectivity removal of trace elements bound to operational defined sediment fraction (Tessier et al., 1979). Partitioning of heavy metals involves the fractionation of the total content into exchangeable, acid extractable (carbonate bound), reducible (Fe-Mn oxides bound), oxidizable (organic bound) and residual forms. The exchangeable and acid extractable fractions are mobile fractions and easily available. The oxidizable and reducible forms are leached out only under extreme conditions, while the residual fraction is almost inert.

The objectives of the present work were to determine the mobility of metals in tailing from Sasa Pb and Zn mine and to evaluate the potential environmental risk of material due to leaching potential of metals.

Materials and Methods

Geology and environmental setting of the study area

The Sasa lead-zinc deposit lies within the Sasa-Toranica mining district in the Osogovo Mountains, eastern Macedonia. The geology of the Toranica-Sasa ore field comprises various rocks of both metamorphic and igneous origin, with the latter of Tertiary age. The most abundant lithologies in the area are believed to be closely associated with mineralization. The Sasa deposit consists of pen concordant tabular ore bodies that wedge out following a transition to non-mineralized metasomatites and lens-sheeted ore bodies. The most economically valuable mineralization is closely-related to that of quartz-graphite schists, with the ore consisting mainly of galena, sphalerite, chalcopyrite and pyrite. Further studies have revealed more details as to the complexity of the deposit's mineralogy, including the presence of galena, sphalerite, chalcopyrite, pyrite, pyrrhotite, magnetite, martite, bornite, enargite, tetrahedrite, marcasite, barite, native gold, cubanite and native bismuth (Serafimovski and Aleksandrov 1995; Stojanov et al. 1995; Serafimovski et al. 2006).

Mining in the region is carried out following the conventional underground method. Mine tailings produced from the milling process are discharged into a tailings pond as slurry. Both tailings and milling material are weakly cemented and locally exposed to weathering, thus promoting the production of AMD and posing a severe threat in terms of trace metal pollution to both the immediate area and those further downstream (towards the River Kamenica and Lake Kalimanci). Running through the Sasa Mine, the River Kamenica receives waste discharge from the mine before finally flowing into Lake Kalimanci.

Sampling and samples preparation

Samples from Sasa tailings dam were taken in May 2011. Samples were collected using a plastic spade, transferred to pre-cleaned plastic bags and then stored in the laboratory at 4 ^{o}C. After collection, samples were oven dried before undergoing dry sieving at a temperature of 50 °C for 48 hours until a constant weight was attained. After being sieved through a 0.315 mm polyethylene sieve to remove plant debris, samples were finally homogenized to a fine powder in a mechanical agate grinder for subsequent analysis.

Pedological analysis of soil and determination of metal mobility

The pH value of tailing was determined according to SIST ISO 10390:1996 in a 0.01 M $CaCl_2$ suspension (liquid to soil ratio 5:1). Reduction potential (E_h) of moist tailing sample was determined by Mettler Toledo combined InLab redox electrode (Pt, Ag/AgCl). A TOC5000A Shimadzu Analysator with solid sample combustion unit (Kyoto, Japan) was used for the determination of total organic carbon in tailing.

To determine the total metal concentration in tailing, the homogenized sample was first dried at 105 °C, powdered and sieved through a 0.250 mm test sieve. Approximately 0.5 g of tailing sample was digested in a mixture of 6 mL HCl, 2 mL HNO_3 and 2 mL of HF (all TraceSelect). Decomposition of sample was performed in closed Teflon vessel at 250 °C for 6 hours and let to cool down to room temperature. For complexation of HF, 22 mL of 4 % boric acid was added and digestion procedure was further performed for 2 h. Digestion of the sample was performed in triplicate, including six blank samples. The certified reference material BCR-143R (Sewage Sludge Amended Soil) was used to check the accuracy of the analytical procedures. The concentration of metals in digested diluted samples was analysed by an Agilent 7500ce series ICP-MS instrument. The standard addition technique (N = 10) was used to avoid matrix interferences. The limit of detection (LOD) was calculated as the concentration corresponding to three times the standard deviation (3s, N=6) of the blank determinations. The accuracy based on the standard reference material was greater than 95 %.

Determination of the mobility of metals in tailing

The mobility of metals was evaluated according to the SIST EN 12457–4 one–stage batch test and Toxicity Characteristic Leaching Procedure – TCLP (USEPA, 2008). Extraction of metals from samples with water and 0.11 M acetic acid was carried out in 30 mL polypropylene centrifugation tubes (Sarstedt, Germany). Ten mL of Milli-Q water (Milli-Q water purification system, Millipore Corp., USA) or 20 mL of 0.11 M acetic acid (pH = 2.83) were added to 1.000±0.005 g of air-dried tailing samples. Samples were shaken for 24 hours at 150 rpm, centrifuged at 3500 rpm for 20 min, decanted and filtered through a cellulose nitrate filter (Sartorius, Germany) of 0.45 µm pore size. Extraction of samples was performed in triplicate with six blank samples for each series.

Fractionation of metals in tailing was determined according to the Tessier's five step sequential extraction procedure (Tessier et al., 1979). During Tessier's sequential extraction procedure, the metals were extracted into five fractions: exchangeable fraction (T1), acid soluble fraction (T2), reducible fraction (T3), oxidizable fraction (T4) and residual fraction (T5). Samples used for metal fractionation determination were first dried at 105 °C, powdered and sieved through a 0.250 mm test sieve. The extraction was performed in 50 mL polypropylene centrifugation tubes. The supernatant was removed with a pipette and filtered through a membrane filter of 0.45 µm pore size. After each extraction step 8 mL of Milli-Q water was added to the residue, centrifuged for 30 min at 3500 rpm and the supernatant discharged. Metal concentrations in extraction solutions were determined with ICP-MS. Water used in preparing stock solutions was obtained from a Millipore Milli-Q Ultrapure Water Purification System. All reagents used for the sequential extraction procedure were of analytical grade. Extraction of samples was performed in six parallels with six blank samples for each series.

The modified version of four-step procedure proposed and validated by the BCR (The European Community Bureau of Reference) was applied for comparison (Sahuquillo et al., 1999). During the procedure the metals were extracted into four fractions: acid soluble fraction (B1), reducible fraction (B2), oxidizable fraction (B3) and residual fraction (B4). To check the accuracy of the analytical procedures, the certified reference material BCR-701 was used.

Results and Discussion

The results of the pedological analysis showed a slightly alkaline reaction of tailing (pH 7.9) with moderately reduced to oxidized redox potential (E_h = 380 mV). Total organic carbon content was <1 %. Total, acetic acid and water extractable metal concentrations in the tailing sample and the corresponding critical legislative concentrations are presented in Table 1.

The total concentrations of Zn, As and Pb significantly exceeded the critical levels of dangerous substances in the soil stated in Slovenian legislation (OGRS, 1996). The concentrations of metals in water extracts were far below the legal limits (OGRS, 2008). The low water soluble concentrations can be attributed to the long period of tailing deposition thus water extractable metal species had already been leached from the tailing during this time. The mobility of all metals, evaluated by TCLP, was also quite low, except of Pb that acetic acid extractable concentration represented 20 % of the total metal concentration (USEPA, 2008) and exceed the TCLP regulatory limits - by a factor of almost seven.

Table 1. Total, water and acetic acid extractable metal concentrations in tailing sample and the corresponding legislative concentrations. Results are presented as the mean of triplicates ± standard deviation.

	As	**Cd**	**Pb**	**Zn**	**Cu**	**Cr**	**Co**	**Ni**
Total conc. [mg kg^{-1}]	93±11	12±1	3318±66	2423±86	211±11	37±3	15±1	33±3
OG RS, 68/1996* [mg kg^{-1}]	55	12	530	720	300	380	240	210
TCLP conc. [mg L^{-1}]	0.018±0.005	0.085±0.004	34±3	4.4±0.5	0.12±0.01	<0.005	0.024±0.002	0.125±0.011
US EPA, SW-846 [mg L^{-1}]	5	1	5			5		
Aqua conc. [mg L^{-1}]	<0.001	<0.001	0.031±0.01	<0.001	<0.001	<0.001	<0.001	<0.001
OG RS, 34/2008 [mg L^{-1}]	0.3	0.03	0.3	18	0.6	0.3	/	0.6

*critical levels

Results of sequential extraction procedures

Two established sequential extraction method (five step Tessier's scheme and four step BCR scheme) were evaluated for trace metal partitioning in Sasa mine tailings. Theoretically the metal fraction realised in the first step of BCR extraction scheme (acid soluble fraction) should correspond to the sum of metal fractions realised in first two steps of Tessier's scheme (exchangeable and acid soluble fraction). In the both schemes more or less the same extractants are applied in order of increasing reactivity, but the S/L ratio and time of extraction are quite different. Due to different experimental conditions, the metal contents found are different. In the literature a few comparison have appeared where the performance of both schemes has been evaluated (López-sánchez et al., 1993; Raksasataya et al., 1996; Anju and Banerjee, 2010). It has been demonstrated that especially the reducing agent used in the Tessier's scheme displays a greater extraction capacity than that of BCR. The main reason is probably in quite higher temperature of extraction used in the Tessier's fractionation scheme.

According to our results (Figure 1 and 2), the most remarkable difference between Tessier's and BCR schemes lies in the first BCR fraction in comparison with the sum of first two fractions at Tessier's scheme. Although the same extractant was used in second step of Tessier's scheme and in the first step of BCR scheme, the ratio S/L is completely different.

By far the most mobile metal in Sasa mine tailing is Pb. The Pb fraction realised in the first step of BCR extraction scheme represent 50 % of total metal concentration whereas the sum of Pb fractions realised in first two steps of Tessier's scheme represent 60 % of total metal concentration. The Pb association with different fractions of BCR scheme decrease in the order: B1 > B4 ~ B3 ~ B2, whereas the fractionation pattern of Pb at Tessier's scheme is T2 > T3 > T5 > T4 > T1. High mobility potential was also observed at Cd that showed the highest association with oxidizable fraction (67 % in BCR scheme and 33 % in Tessier's scheme) with fractionation pattern B3 > B4 > B1 > B2 and T4 > T3 > T2 > T3 > T1, respectively.

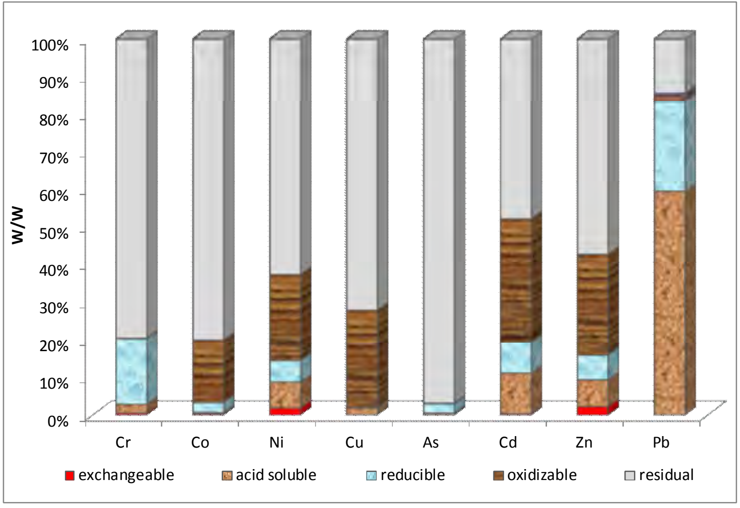

Fig.1: Partitioning of metals in tailing according to Tessier's scheme

In Sasa mine tailing Zn is mainly associated with residual fraction (57 % in both extraction schemes) and oxidizable fraction (37 % at BCR and 27 % at Tessier's scheme). Co, Ni and Cu are mainly associated with oxidizable and residual fraction whereas Cr is predominantly partitioned between the residual (87 % at BCR and 97 % at Tessier's scheme) and reducible fraction (9 % at BCR and 17 % at Tessier's scheme). According to the ratio of residual fraction, As shows the lowest mobility among studied metals.

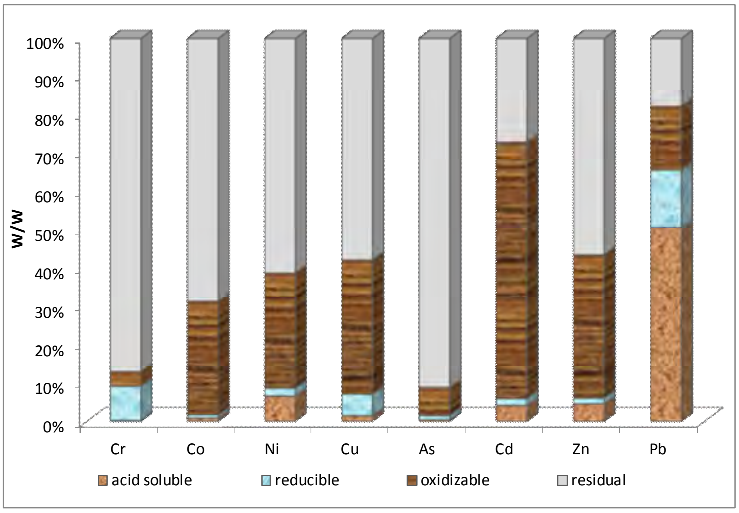

Fig.2: Partitioning of metals in tailing using modified BCR extraction scheme

Conclusion

Data from this partitioning study indicate that Pb is the most mobile metal in Sasa mine tailing since only 15 % of total Pb is associated with residual fraction with 50 % of total Pb found in acid soluble fraction. By far less mobility according to the first step of BCR scheme showed Ni, Cd and Zn with acid soluble concentration less than 7 %. Results shown that due to high mobility of metals, tailings from Sasa mine represent a serious threat to the surrounding environment. Further research activity is urgent to find a potential remediation strategy to reduce the metal mobility in tailing.

References

Anju, M., Banerjee, D.K., 2010. Comparison of two sequential extraction procedures for heavy metal partitioning in mine tailings. Chemosphere 78, 1393-1402.

Dermatas, D., Shen, G., Chrysochoou, M., Grubb, D.G., Menounou, N., Dutko, P., 2006. Pb speciation versus TCLP release in army firing range soils. Journal of Hazardous Materials 136, 34-46.

López-sánchez, J.F., Rubio, R., Rauret, G., 1993. Comparison of Two Sequential Extraction Procedures for Trace Metal Partitioning in Sediments. International Journal of Environmental Analytical Chemistry 51, 113-121.

McGowen, S., Basta, N., 2001. Heavy Metal Solubility and Transport in Soil Contaminated by Mining and Smelting. Heavy Metals Release in Soils. CRC Press, pp. 89-107.

OGRS, 1996. Decree on limit values, alert thresholds and critical levels of dangerous substances in soil, vol. 68/1996, amendment 41/2004

OGRS, 2008. Decree on burdening of soil with waste spreading, 2008, vol. 34/2008.

Quevauviller, P., Rauret, G., López-Sánchez, J.F., Rubio, R., Ure, A., Muntau, H., 1997. Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. Science of The Total Environment 205, 223-234.

Raksasataya, M., Langdon, A.G., Kim, N.D., 1996. Assessment of the extent of lead redistribution during sequential extraction by two different methods. Analytica Chimica Acta 332, 1-14.

Ruby, M.V., Davis, A., Schoof, R., Eberle, S., Sellstone, C.M., 1996. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. Environmental Science & Technology 30, 422-430.

Sahuquillo, A., López-Sánchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., Ure, A.M., 1999. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. Analytica Chimica Acta 382, 317-327.

Serafimovski T., Aleksandrov M., 1995. Lead and Zinc deposites and occurrences in the Republic of Macedonia (in Macedonian, with extended abstract). Stip, Macedonia: Special edition of the Faculty of Mining and Geology.

Serafimovski T., Dolenec T., Tasev G., 2006. New data concerning the major ore minerals and sulphosalts from the Pb-Zn Zletovo Mine, Macedonia. RMZ, Materials and Geoenvironment, 52, 535-548.

Stojanov R., Serafimovski T., Boev B., Rakic S., 1995. Magmatic activity and Metalogeny in the Northern parts of the Zletovo-Kratovo Ore District. Paper presented at the International Workshop, UNESCO-IGCP Project 356, Stip, Macedonia.

Tessier, A., Campbell, P.G.C., 1988. Comments on the testing of the accuracy of an extraction procedure for determining the partitioning of trace-metals in sediments. Analytical Chemistry 60, 1475-1476.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace-metals. Analytical Chemistry 51, 844-851.

USEPA, 2008. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Analytical Method 1311: Toxicity Characteristic Leaching Procedure. Washington, DC.

TRANSFER FACTOR EVALUATION IN THE KOČANI FIELD SOIL-PLANT SYSTEM (REPUBLIC OF MACEDONIA)

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Abstract

This investigation focuses on transfer factor values in the Kočani Field soil - plant system (Republic of Macedonia). To identify the heavy metal concentrations transfer characteristics in Kočani crops (rice and maize), the transfer factor (TF) values were calculated. High transfer factor values for Mo, Zn, Cd and Cu revealed a strong accumulation of Mo, Zn and Cd by rice, and Mo and Zn by maize crops. The pattern of the TF values in our study decreased with increasing total metal concentrations in soils, indicating an inverse relationship between TF and total metal concentrations in soils.

Keywords: heavy metals, transfer factor, rice, maize, Kočani Field, Republic of Macedonia

1. Introduction

Soil is a specific component of the biosphere because it is not only treated as a geochemical sink for contaminants, but also as a natural buffer system controlling the transport of chemical elements and substances into the biota, hydrosphere and atmosphere. It has always been important for humans and their health, especially as a resource that can be used for shelter and food production.

Kočani Field has a long history of base-metal mining (Pb-Zn Zletovo-Kratovo and Sasa-Toranica ore districts), and paddy rice (*Oryza sativa L.*) and maize (*Zea mays L.*) are some of the main agricultural products in the region. Previous study has shown that the riverine water from the Zletovska and Bregalnica Rivers, which are used to irrigate the Kočani (paddy and maize) fields, is contaminated with heavy metals as a result of the inflow of acid mine water and untreated effluents from the ore processing facilities (Zletovo-Kratovo and Sasa-Toranica ore district) (Alderton et al. 2005). Metals usually enter agricultural soils through irrigation processes (Chen et al. 1997), and for this reason agricultural soil and plant crops can also be contaminated, introducing a risk to human and animal health. In this context, the major aims of the present study is to estimate the heavy metal uptake by food crops by transfer factor assessment.

1.1. Transfer factor (TF) from soil to crop

The soil-to-plant transfer is one of the key components of human exposure to metals through the food chain. To investigate the transfer of heavy metals from soil to crops, the transfer factor (TF) values of heavy metals studied were calculated as follows (Cui et al. 2004):

$TF = C_{crop} / C_{soil}$,

where C_{crop} and C_{soil} signify heavy metal concentration in the crops (rice, maize) and paddy soils, where the crops are grown on a dry weight basis, respectively. In this study, we used the mean concentration values of heavy metals determined in crops (rice, maize) and paddy soils.

2. Materials and methods

2.1. Study area

Kočani Field is located in eastern Macedonia, about 32 km from the city of Štip and 115 km from the capital city Skopje. With an average length of 35 km and width of 5 km, Kočani Field lies in the valley of the Bregalnica River, between the Osogovo Mountains in the north and Plačkovica Mountains in the south (see Fig. 1).

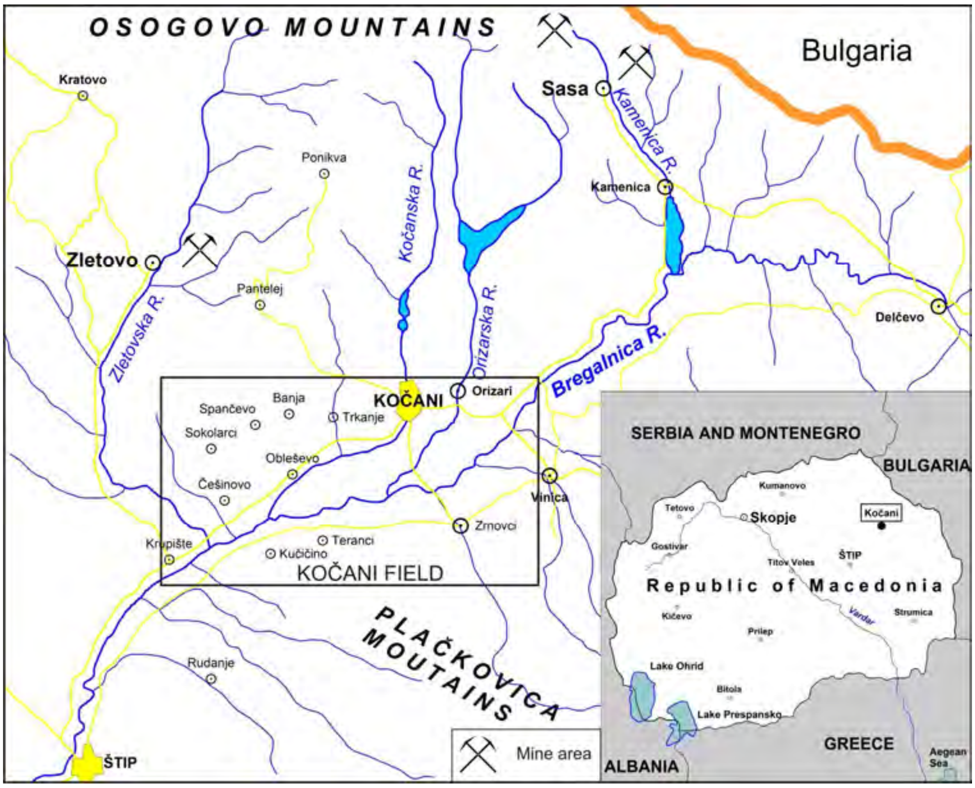

Fig. 1: Study area, Kočani Field (Dolenec et al. 2007).

The region is well known as an agricultural and mining province, with significant thermal activity. Hot thermal waters are very convenient for warming greenhouses. The most important agricultural products in the region are rice, maize, tomatoes, cucumbers, red peppers and other vegetables. The centre of the region, the city of Kočani, was founded on the southern foothills of the Osogovo Mountains. The municipality of the Kočani area comprises 28 settlements with 38,092 inhabitants.

Rice grain samples (*Oryza sativa* L.) with hulls were collected during harvesting in November 2005 from 14 sampling sites across Kočani Field. Selected sampling points were located at the same approximate positions as the corresponding soil sample locations. Maize grains (*Zea mays* L.) were sampled during harvesting in October 2008 from 15 sampling locations over Kočani Field. Sampling locations were chosen near the corresponding soil and rice samples locations.

2.2. Statistical analysis

To investigate the elemental associations among the analysed elements in rice and maize samples, Pearson *R* correlation analyses were applied to all samples studied. Critical values of the correlation coefficients (r) were: 0.36 at $p \leq 0.05$, 0.43 at $p \leq 0.01$, 0.93 at $p \leq 0.005$ and 0.91 at $p \leq 0.001$. Results that yielded $p \leq 0.05$ were considered borderline significant, whereas those at $p \leq 0.01$ were denoted significant. Results at $p \leq 0.005$ or $p \leq 0.001$ levels were evaluated as highly significant.

The basic statistical parameters for each element and the statistical calculations mentioned above were computed by the statistical software program, Statistica VI.

3. Results and discussion

3.2. Transfer factor (TF) from soil to crop (rice and maize)

Figures 2 and 3 show the TF values calculated for heavy metal transfer from soils to rice and maize grains.

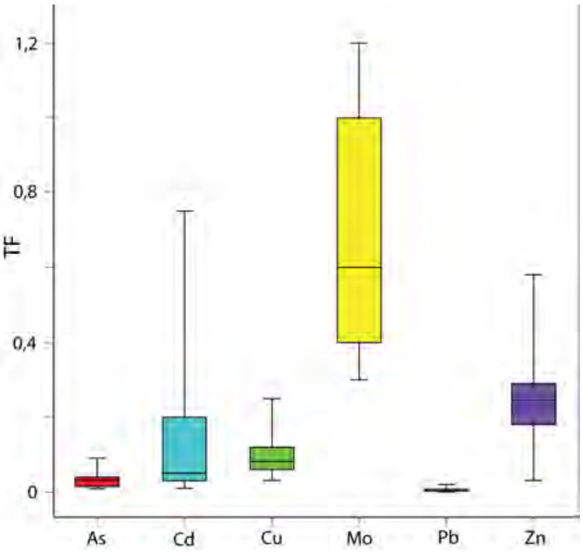

Fig. 2. TF values for heavy metals in rice samples.

For an individual heavy metal, the TFs vary greatly within the plant species (Cui et al. 2004). There was a significant difference in TF values among the rice and maize crops. The TF values for heavy metals in maize samples were generally lower, principally because the heavy metal concentrations detected were also lower than those in the rice grains (Rogan Šmuc 2010).

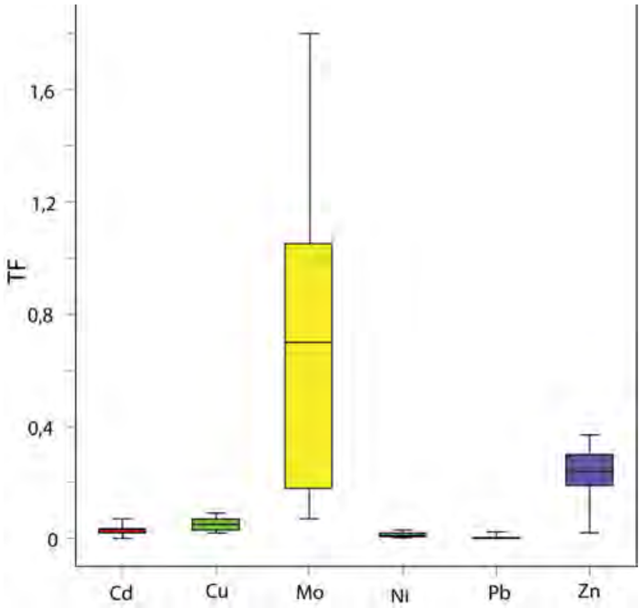

Fig. 3. TF values for heavy metals in maize samples.

Mean TF values for heavy metals, including As, Cd, Cu, Mo, Pb and Zn in rice samples, were 0.03, 0.15, 0.1, 0.7, 0.01 and 0.37, showing medium accumulation (TF = 0.01-1.0). The trends in the TF values for heavy metals in rice crops were in the following descending order: Mo > Zn > Cd > Cu > As > Pb. The results for TF values of maize crops were 0.03 for Cd, 0.05 for Cu, 0.76 for Mo, 0.01 for Ni, 0.004 for Pb and 0.2 for Zn, respectively. These values signify slight (TF = 0.001-0.01) and medium accumulation (TF = 0.01-1.0). The trends for the TF for heavy metals in maize crops were in order of Mo > Zn > Cu > Cd > Ni > Pb. The higher the TF values are, the more mobile/available the metal is (Dean 2008). Therefore, the high TF values for Mo, Zn, Cd and Cu revealed a medium accumulation of Mo, Zn and Cd by rice, and Mo, Zn and Cu by maize crops.

Similarly, we performed Pearson's correlation analysis to identify the relationships between the heavy metal concentrations in soil (Rogan Šmuc 2010) and rice samples (Table 1). Highly positive correlations were established for As, Cd, Cu, Pb and Zn, whereas there was no association present with Mo and other heavy metals. The results revealed that, in soil and rice samples, As, Cd, Cu, Pb and Zn have similar geochemical characteristics and behaviour. The correlation between Mo and other heavy metals determined in soil and rice samples was insignificant.

Table 1. Pearson's correlation matrix for relationship among total heavy metals content in paddy soil and unpolished rice samples (marked correlations are significant at $p < 0.05$).

Rice\Soil (S)	**As (S)**	**Cd (S)**	**Cu (S)**	**Mo (S)**	**Pb (S)**	**Zn (S)**
As	**0.73**	**0.73**	**0.61**	**0.79**	**0.73**	**0.72**
Cd	**0.89**	**0.84**	**0.76**	**0.89**	**0.83**	**0.84**
Cu	**0.64**	**0.63**	**0.61**	**0.71**	**0.63**	**0.63**
Mo	0.50	0.48	0.51	**0.57**	0.49	0.49
Pb	**0.85**	**0.86**	**0.86**	**0.85**	**0.86**	**0.87**
Zn	**0.82**	**0.80**	**0.69**	**0.81**	**0.79**	**0.79**

Table 2 presents the relationship between heavy metal content in soil (Rogan Šmuc 2010) and maize samples. The correlation matrix exhibited significant correlations for Cd with Cu, Mo, Pb and Zn and for Zn with Cu, denoting their similar geochemical characteristics and behaviour in soils and maize grains from Kočani Field. Negative and insignificant relationships were observed with all other heavy metals present in soil and maize samples.

Table 2. Pearson's correlation coefficients for relationship between total heavy metals concentrations in paddy soil and maize samples (marked correlations are significant at $p < 0.05$).

Corn\Soil (S)	**Cd (S)**	**Cu (S)**	**Mo (S)**	**Pb (S)**	**Zn (S)**	**Ni (S)**
Cd	**0.53**	-0.04	-0.23	0.04	0.36	-0.10
Cu	**0.62**	-0.01	-0.34	-0.04	**0.52**	-0.17
Mo	**0.64**	-0.17	-0.26	-0.03	0.29	-0.21
Pb	**0.55**	-0.05	-0.22	0.04	0.37	-0.12
Zn	**0.54**	-0.05	-0.23	0.03	0.37	-0.11
Ni	-0.39	0.17	-0.33	-0.07	-0.13	0.24

Generally, the TF results (Mo > Zn > Cu > Cd > Ni > Pb) confirmed the sequential extraction results, where the mobility of the heavy metals studied was estimated to be in the following order: Cd > Mo > Sb > Zn > Cu > As > Pb > Ni > Ag (Rogan Šmuc 2010).

It was interesting why the TF values for Mo and Zn prevailed over Cd, especially if we compare them with the results of the sequential extraction study. In particular, no direct evidence exists about Mo active uptake. Mo is moderately mobile in plants, but the form of Mo translocation is unknown (Kabata-Pendias and Pendias 2001). However, the paddy soils studied were characterized as well-aerated (oxidizing) acid soils (pH = 5.5) (Rogan Šmuc 2010), which means that Mo could be easily mobile and available to plants (Rose et al., 1979). Roots often contain much more Zn than plant tops, but with the luxury levels of soil Zn might translocate from the roots and accumulate in the plant tops (Kabata-Pendias and Pendias 2001). On the contrary, a greater proportion of Cd is known to accumulate in root tissues, although Cd present in plants is relatively mobile (Kabata-Pendias and Pendias 2001). As there is no information about the heavy metal concentrations present the rice and maize roots, we concluded that: (1) according to the other elements studied, Mo was highly mobile in the plants growing in the Kočani Field area; (2) very high amounts (luxury levels) of Zn were measured in the Kočani paddy soil

(Rogan Šmuc 2010) and the translocation process from roots to plant grains easily occurred; and (3) with regard to the total Cd amounts and the mobility characteristics in paddy soils (Rogan Šmuc 2010), Cd was mostly accumulated in the plant roots.

The pattern of the TF values in our study decreased with increasing total metal concentrations in soils, indicating an inverse relationship between TF and total metal concentrations in soils. This was also recognised by Khan et al. (2008) and Wang et al. (2006).

4. Conclusions

High TF values for Mo, Zn, Cd and Cu revealed a medium accumulation of Mo, Zn and Cd by rice, and Mo, Zn and Cu by maize. The TF results generally confirmed the sequential extraction results, but with regard to the differences we discovered the following: (1) Mo was highly mobile (according to the other elements studied) in the plants growing in the Kočani Field area; (2) in the Kočani Field plant samples the translocation process of Zn from soils, roots to plant grains had occurred; and (3) Cd was probably mostly accumulated in the plant roots.

According to the results, the area around Zletovska River is considered to be the most anthropogenically impacted part of Kočani Field region. Thus, an urgent and systematic study on heavy metal concentrations in drinking water and other edible crops in Kočani Field area is essential.

Acknowledgements

The research was supported financially by the Slovenian Research Agency (ARRS), contract number 1000-05-310229.

5. References

Alderton, D. H. M., Serafimovski, T., Mullen, B., Fairall, K., James, S., et al. (2005). The chemistry of waters associated with Metal Mining in Macedonia. *Mine water Environment*, 24, 139-149.

Chen, T. B., Wong, J. W. C., Zhou, H. Y., Wong, M. H., et al. (1997). Assessment of trace metal distribution and contamination in surface soils of Hong Kong. *Environmental Pollution*, 96, 61-68.

Cui, Y. J., Zhu, Y. G., Zhai, R. H., Chen, D. Y., Huang, Y. Z., Qui, Y., et al. (2004). Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. *Environment International*, 30(6), 785-91.

Dean, J. R. (2008). *Bioavailability, Bioaccessibility and Mobility of Environmental Contaminants*. 1 st ed. England; John Wiley and Sons Ltd.

Kabata-Pendias, A., & Pendias, H. (2001). Trace Elements in Soils and Plants. 3rd ed. Boca Raton; CRC Press.

Khan, S., Cao, Q., Zheng, Y. M., et al. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*, 158, 686-692.

Rogan Šmuc, N. (2010). *Heavy metal contamination of soils and crops in teriary basins: a case study of Kočani Field (Macedonia)*. Dr thesis, 108 pp.

Wang, G., Su, M. Y., Chen, Y. H., et al. (2006). Tranfer characteristics of cadmium and lead to the edible parts of six vegetable species in southeastern China. *Environmental Pollution*, 144, 127-135.

GEOCHEMICAL CHARACTERIZATION OF LEAD AND ZINC IN SURFICIAL LAKE SEDIMENTS (LAKE KALIMANCI, REPUBLIC OF MACEDONIA)

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Abstract

In the present study surficial lake sediments were analyzed at a certified Canadian laboratory (Acme Analytical Laboratories) via ICP-MS, with all geochemistry data processed using the Statistica 8 software program. In order to assess environmental pollution status, two environmental factors were established, while for the determination of chemical speciation of toxic metals a sequential extraction procedure was carried out. Concentrations of lead and zinc in surficial Lake Kalimanci sediments ranged from 4863-16300 and 7056-20900 μg g^{-1}, respectively. Based on values of the enrichment factor and geoaccumulation index, surficial sediment from Lake Kalimanci is strongly polluted with lead and zinc. The results of the sequential extraction procedure revealed lead and zinc are strongly bonded to the exchangeable fraction. The geochemistry, environmental factor values and toxic metal extraction characteristics of Lake Kalimanci sediments represent a serious environmental risk for an extensive area.

Key words: lead and zinc contamination, sequential extraction procedure, surficial lake sediments, Lake Kalimanci, Republic of Macedonia.

Introduction

Toxic metals are the most widespread pollutants which originate from industrial activities, particularly from mining and smelting waste sites (e.g. Salomons 1995; Hochella et al. 2005). Through ore extraction and processing, large amounts of waste material (containing toxic metals) are produced and stored, much of it highly toxic. Toxic metals in the surficial sediments of natural and artificial lakes or water-storage facilities are mostly associated with fine-grained particles. Contaminated lake sediments are generally regarded as an important component of the overall lake system, since they provide a bank of environmental information regarding the extent of both natural and anthropogenic pollution (Dauvalter and Rognerud 2001; Belzile et al. 2004; Das 2005; Bibi et al. 2007). The mobility and bioavailability of toxic metals and other elements stored in lake bottom sediments depend on many different factors, such as temperature, pH, pressure, salinity, the chemical form of the element and redox conditions (Jernström et al. 2010). However, due to their rapid sedimentation rates, the sediments of water-stores are often considered to be little affected by early-stage diagenetic processes (Callender 2000) and thus provide a well-preserved and well-documented history of toxic metal input derived from, for instance, a catastrophic spillage of acid-mine tailings into the adjacent environment.

The current study is the first to investigate not only the concentrations of Pb and Zn present in the surficial sediment of the artificial mine which has impacted Lake Kalimanci in eastern Macedonia, but also the chemical form in which they occur using sequential extraction. The results are combined in order to more accurately define the enrichment of toxic metals derived from the massive acid-mine tailings spill which took place in 2003. The environmental risk associated with total toxic metal concentrations and their geochemical fractionation in sediment will also be evaluated.

2 Materials and Methods

2.1 Geology and environmental setting of the study area

Situated in eastern Macedonia, Lake Kalimanci lies in the vicinity of the small town of Makedonska Kamenica, about 5 km from the Sasa-Toranica ore district (Fig. 1). With a length of 14 km and width of 0.3 km, the lake covers an area of 4.23 km^2 and contains approximately 127 million m^3 of water. The basic purpose of Lake Kalimanci is the storage of water which is used to irrigate around 30,000 hectares of mainly rice fields in the Kočani Valley and Ovce Pole.

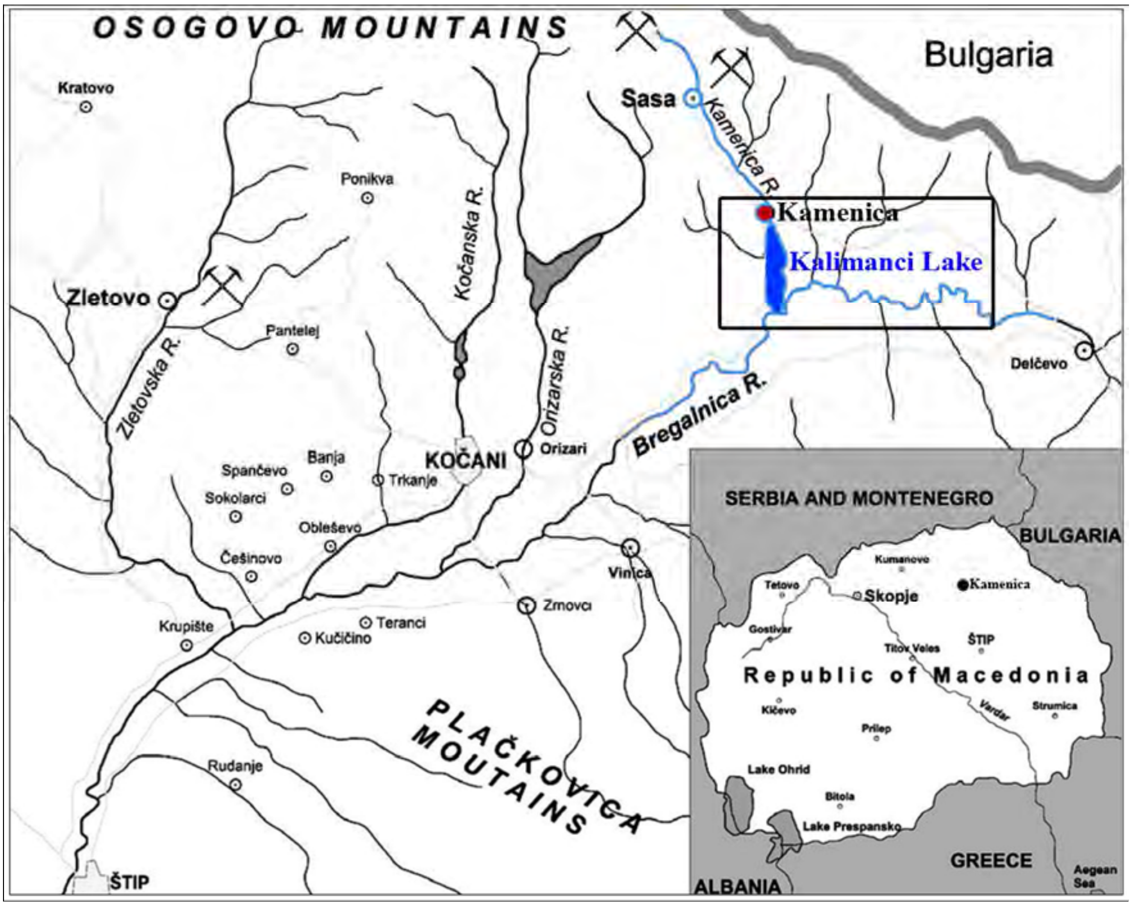

Fig. 1 Geographical location map of Lake Kalimanci.

The Sasa lead-zinc deposit lies within the Sasa-Toranica mining district in the Osogovo Mountains, eastern Macedonia. The geology of the Toranica-Sasa ore field comprises various rocks of both metamorphic and igneous origin, with the latter of Tertiary age. The most economically valuable mineralization is closely-related to that of quartz-graphite schists, with the ore consisting mainly of galena, sphalerite, chalcopyrite and pyrite.

Sampling methods

Seven surface sediment samples were collected from Lake Kalimanci in September 2008 (Fig. 2), with sample pH values ranging from 5.5 to 7.5. Sampling was carried out during a dry period (no precipitation-summer season) when the lake water levels were lower and the sediment exposed to oxidation processes. Samples were collected using a plastic spade, transferred to pre-cleaned plastic bags and then stored in the laboratory at 4 °C. After collection, samples were oven dried before undergoing dry sieving at a temperature of 50 °C for 48 hours until a constant weight was attained. After being sieved through a 0.315 mm polyethylene sieve to remove plant debris, samples were finally homogenized to a fine powder in a mechanical agate grinder for subsequent analysis.

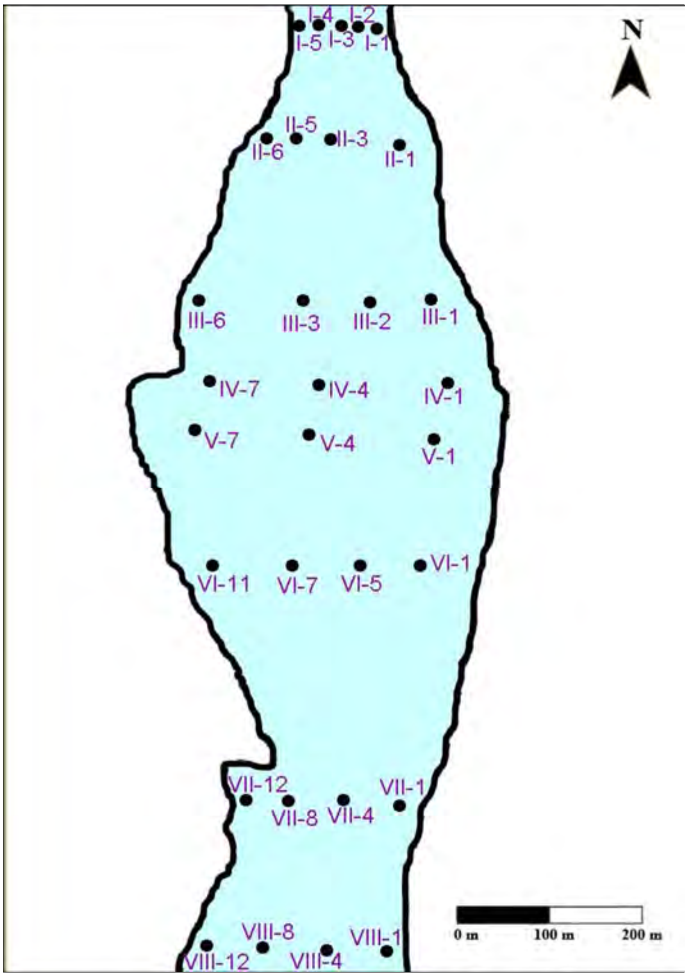

Fig. 2 Distribution of sampling stations across Lake Kalimanci.

Sediment samples were analyzed for major and trace element concentrations at a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd – Ontario, Canada) using a variety of different analytical methods. After extraction of sub-samples for 1h with 2-2-2-HCl-HNO_3-H_2O at 95 °C, lead and zinc were analyzed via ICP-MS. The analytical precision and accuracy were both better than ± 6%, as indicated by the results of duplicate measurement of 3 lake samples and of the MAG-1 standard.

The obtained results were then analyzed using linear regression and analysis of covariance (ANCOVA) in the Statistica 8 software program. The 95% confidence intervals were employed for regression calculations.

The use of a global mean in the examination of regional or local anthropogenic metal contamination has limitations (Matschullat et al. 2000). In order to differentiate between the lithogenic and anthropogenic origin of toxic metals in Lake Kalimanci sediments, toxic metal concentrations were normalized to Sc.

In order to evaluate the extent of toxic metal pollution affecting Lake Kalimanci sediments, an enrichment factor (EF) was calculated as follows:

$$EF = (Me/Sc)sed\,/(Me/Sc)\ sed\ Dojran;$$

where (Me/Sc)sed is the concentration ratio of a given metal to Sc in the Kalimanci sediment sample, and (Me/Sc) sed Dojran the average ratio of the same metal to Sc in the reference (non-polluted – sed. Dojran) Lake Dojran (Macedonia), in the vicinity of which no mining activity takes place.

Enrichment factor values can be interpreted as representing the level of toxic metal pollution as suggested by Birth (2003), with the assessment criteria based on the EF values presented in Table 1.

Table 1. Enrichment factor (EF) value in relation to pollution intensity as suggested by Birth (2003).

EF<1	indicates no enrichment
1<EF<3	minor enrichment
3<EF<5	moderate enrichment
5<EF<10	moderately severe enrichment
10<EF<25	severe enrichment
25<EF<50	very severe enrichment
EF>50	extremely severe enrichment

2.5.2 Geoaccumulation index (I_{geo})

A second criterion with which to evaluate the intensity of historical toxic metal pollution of Kalimanci sediments is the geoaccumulation index devised by Müller (1979) and Förstner and Müller (1973):

$$I_{geo} = log2\quad ((M)sed\,/\,1.5(M)sed\ Dojran),$$

where (M)sed is the concentration of a given toxic metal and (M)sed Dojran is the mean concentration of the same metal in the sediments of the reference site (Lake Dojran). The I_{geo} is associated with a qualitative scale of pollution intensity, as shown in Table 2.

Table 2. Geoaccumulation index (I_{geo}) in relation to pollution intensity after Müller (1979).

I_{geo}	Pollution intensity
>5	very strongly polluted
4-5	strongly to very strongly polluted
3-4	strongly polluted
2-3	moderately to strongly polluted
1-2	moderately polluted
0-1	unpolluted to moderately polluted
<0	unpolluted

The trace metal content of different chemical fractions of the samples was determined via various extractions of lake sediment components. In order to estimate pollutant speciation and bioavailability in the sediment samples, a sequential extraction method devised by ACME laboratories was applied. The most commonly-isolated phases in such sequential extraction schemes include a water-soluble fraction (leaching stage 1), an exchangeable + carbonate fraction (leaching stage 2), an oxidizable - organic fraction (leaching stage 3), an Fe–Mn oxide bound - reducible fraction (leaching stage 4) and a residual + reducible fraction (leaching stage 5).

Table 3. Sequential extraction procedure – fractions and chemical reagents.

Step	Fraction	Reagents/1 g sample
1	water soluble	20 ml distilled water
2	exchangeable and carbonate bound	20 ml ammonium acetate
3	organic (oxidizable)	20 ml 0.1 M sodium pyrophosphate ($Na_3P_2O_7$)
4	reducible	60°C, 20 ml 0.1 M hydroxylamine hydrochloride
5	reducible plus residual	90°C, 20 ml 0.25 M hydroxylamine hydrochloride

3 RESULTS and DISCUSSION

Total toxic metal concentration and comparison of individual toxic metal concentrations with natural background values and other lakes

The present study focuses on changes in the concentration and chemical fractionation of lead and zinc in Lake Kalimanci sediments, with the aim of identifying the dispersal of toxic metals by riverine transport from Sasa mine. At Lake Kalimanci most mining waste material is retained behind a dam. Seven sediment samples (I-4 to VIII-8) were obtained from the lake along a transect extending from the village of Kamenica to the lake outlet at this dam (Fig. 1). The highest amounts of lead and zinc were measured at location II-3 in the northern part of Lake Kalimanci, with Pb 16300 µg/g, Zn 20900 µg/g.

Table 4. Concentration (c[µg/g]) of lead and zinc in the investigated samples.

Element c [µg/g]	**Pb**	**Zn**
Location		
I-4	9357	10700
II-3	16300	20900
III-3	10900	14000
V-7	9472	12600
VI-11	7557	11600
VII-12	5144	9326
VIII-8	4863	7056
Mean	9085	12312
Min	4863	7056
Max	16300	20900
Std.Dev.	3900	4403

Enrichment factor (EF) and Geaccumolation index (I_{geo})

Calculation of EF values revealed that both studied toxic metals were enriched in surficial Lake Kalimanci sediments. The highest mean EF values were observed for Pb (298.69) and Zn (146.16) (Table 5), representing extremely severe enrichment.

Table 5. Enrichment factor values and geoaccumolation values of lead and zinc.

Location	EF-Pb	EF-Zn	I_{geo}-Pb	I_{geo}-Zn
I-4	357.41	138.46	7.63	6.27
II-3	670.51	291.25	8.43	7.23
III-3	388.59	169.08	7.85	6.65
V-7	337.68	152.17	7.65	6.50
VI-11	269.41	140.10	7.33	6.38
VII-12	171.93	105.59	6.77	6.07
VIII-8	162.53	79.89	6.69	5.66
Average	336.87	153.79	7.48	6.39

The results (average I_{geo} values) reveal surficial Lake Kalimanci sediments (Table 5) to be very strongly polluted with Pb (7.48) and Zn (6.39). This pollution has likely existed since the major environmental disaster of 2003.

Sequential extraction data

The environmental hazard represented by the contamination of Lake Kalimanci surficial sediments not only depends on the total metal content, but also on the latter's mobility and bio-availability, as determined by sequential extraction. The extracted percentage values of Pb and Zn are found in the eight surficial lake sediment samples after each sequential extraction step are shown in Table 3, while Figure 3 shows the percentage of the sum of all fractions.

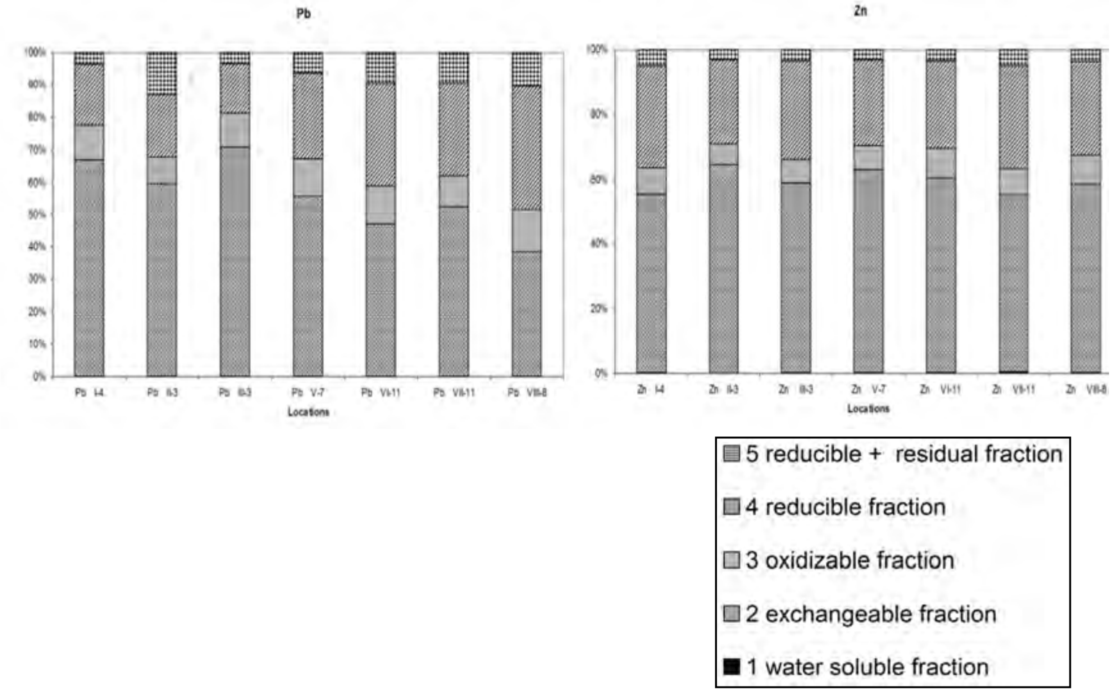

Fig. 3 Percentage of Pb and Zn removed after each step of the sequential extraction procedure applied to sediments from Lake Kalimanci.

Concentrations of Pb measured after the sequential extraction of lake sediments are shown in Figure 3. A large proportion of Pb was bound to the exchangeable fraction (F2), with levels varying from 1383.71 µg/g to 6457.23 µg/g. The highest amounts of extracted Pb were found on the northern side of Lake Kalimanci. Concentrations of lead in the reducible phase (F4) were found to be the greatest along the middle of the lake, at levels ranging between 1003.50-2021.74 µg/g.

A significant amount of Zn - 1647.6-4446 µg/g (locations VII-12 and II-3) - was found in the exchangeable fraction (F2), and the least in water-soluble form (F1) (0.07-0.57 µg/g at the same locations as that of the exchangeable fraction). Zn was also highly mobile in the reducible fraction (F4), with levels varying from 0.95 µg/g at location VII-12 to 1.77 µg/g at location II-3. In the investigated lake sediments, Zn was weakly associated with the oxidizable fraction (F3) and the reducible + residual fraction (F5).

Both elements are highly mobile in the first two fractions (F1, F2) what mean that they are soluble in pure water or, in this case, the weakly acidic (due to high levels of sulphates) water of Lake Kalimanci and are therefore very harmful to the environment.

4 CONCLUSIONS

The present study has reported the results of an investigation into the presence of lead and zinc in Lake Kalimanci sediments. Concentrations of toxic metals such as Pb and Zn, were generally extremely high. Increased concentrations of metals in the northern part of Lake Kalimanci are most likely related to the release of tailings dam material from mining activity at Sasa mine. In the southern part of the lake, the high sediment metal content observed is probably associated with the presence of finer sediments (silt and clay) derived from the inflowing River Kamenica. Based on the EF classification, the magnitude of toxic metal pollution in Lake Kalimanci sediments follows the following ranking: Zn>Pb. A similar order was also determined after calculation of I_{geo} values. The results of a sequential extraction procedure revealed that Pb and Zn are highly mobile in the water soluble and exchangeable fraction, which undoubtedly represents an increased environmental risk.

Acknowledgments

This research was financially supported by the Slovenian Research Agency (ARRS), contract number 1000-09-310079.

References

Belzile N, Chen YW, Gunn JM, Dixit SD (2004) Sediment trace metal profiles in lakes of Killarney Park, Canada: from regional to continental influence. Environ. Pollut. 130: 239–248.

Bibi MH, Ahmed F, Ishiga H (2007) Assessment of metal concentrations in lake sediments of southwest Japan based on sediment quality guidelines. Environmental Geology 52: 625–639.

Birth G (2003) A scheme for assessing human impacts on coastal aquatic environments using sediments. In: Woodcoffe CD, Furness RA (Eds.), Coastal GIS 2003. Wollongong University Papers, Center for Maritime Policy 14, Australia.

Callender E (2000) Geochemical effects of rapid sedimentation in aquatic systems: minimal diagenesis and the preservation of historical metal signatures. J. Paleolimnol. 23: 243–260.

Das BK (2005) Environmental pollution impact on water and sediments of Kumaun lakes, Lesser Himalaya, India: a comparative study. Environ. Geol. 49: 230–239.

Dauvalter V, Rognerud S (2001) Heavy metal pollution in sediments of the Pasvik River drainage. Chemosphere 42: 9–18.

Förstner U, Muller G (1973) Heavy metal accumulation in river sediments: a response to environmental pollution. Geoforum 145: 53–61.

Hochella Jr. MF, Moore JN, Putnis CV, Putnis A, Kasama T, Eberl DD (2005) Direct observation of heavy metal-mineral association from the Clark Fork River Superfund Complex: implications for metal transport and bioavailability. Geochimica et Cosmochimica Acta 69: 1651–1663.

Jernström J, Lehto J, Dauvalter VA, Hatakka A, Leskinen A, Paatero J (2010) Heavy metals in bottom sediments of Lake Umbozero in Murmansk Region, Russia. Environmental Monitoring and Assessment, doi: 10.1007/s10661-008-0730-7.

Matschullat J, Ottenstein R, Reimann C (2000) Geochemical background—can we calculate it? Environ. Geol. 39: 990–1000.

Müller G (1979) Schwermetalle in den sediment des Rheins,Veranderungem Seit 1971. Umschau 79: 778-783.

Salomons W (1995) Environmental impact of metals derived from mining activities: Processes, predictions, prevention. J. Geochem. Explor. 52: 5–23.

USE OF STABLE NITROGEN ISOTOPES COMPOSITION OF PARTICULATE ORGANIC MATTER IN THE COSTAL ENVIRONMENT (ISTRA PENINSULA, NORTHERN ADRIATIC)

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Abstract

Stable nitrogen isotope composition of particulate organic matter (POM) was measured to assess the impact of anthrophogenically derived organic matter along Istra peninsula coast (NW Croatia). The measured $\delta^{15}N$ values in POM reflect enrichment of organic matter near the coast due to untreated municipal sewages of cities and local septic systems. Oppositely, negative $\delta^{15}N$ values reflect the depleted effect of purification plants of Pula and Rijeka cities. Variations of $\delta^{15}N$ between sampling periods can be the result of different amounts of the organic matter during the year and also with the rapid and changeable movement of floating POM material in the water column. The results of $\delta^{15}N$ values observed in POM from Istra coast were also lower than in anthopogenically affected Pirovac Bay and significantly higher than unaffected locations of Koranti Islands (both located in the Central Adriatic).

Key words: particulate organic matter (POM), nitrogen ($\delta^{15}N$) isotope composition, anthropogenic impact, Northern Adriatic

Introduction

Increased nutrient inputs mainly in coastal ecosystems can be often reflected as eutrophication that consequent influence to the aquatic communities. Coastal environments are exposed to anthropogenic nutrient inputs from untreated domestic and municipal sewages, industrial effluents, traffic, tourism, agriculture as well as aquaculture activities (Constanzo et al., 2001; Vizzini and Mazzola, 2006; Dolenec et al., 2006; and many others). Such inputs lead to increased primary production and concentration of particulate organic matter (POM) in the water column, increased abundance of nuisance algae, consequent reduced oxygen content of the water and decimated some other marine organisms (Evgenidou and Vaiela, 2002 and references therein).

Previous studies of stable isotopes, mainly nitrogen $\delta^{15}N$, have shown several marine organisms and POM are usable as a tracers of anthropogenic pollution (Dolenec T. et al., 2006; Dolenec M., et al., 2011 and references therein). It was proved that the POM derived from sewage effluents has higher $\delta^{15}N$ values relative to POM of unaffected marine environments (Fogg et al., 1998) and can be therefore used as a tracer for detecting anthropogenic inputs into the marine coastal ecosystem (Constanzo et al., 2001, Gaston et al., 2004, Dolenec T., 2006, 2007). Particulate organic matter (POM) generally representing a mixture of phyto- and zooplankton, bacteria, and detritus. It is present as a floating material in a larger amount within the coastal water marine column. Due to its physical characteristics it is very mobile using wind, currents and tides.

The aim of this study was to asses the anthropogenic effects on the POM along the Istra Peninsula coast by using nitrogen isotope analysis. For this purpose, samples were collected in coastal areas with different amount of anthropogenic inputs.

Materials and methods

Study area

The investigation area; i.e. coastal area along Istra Peninsula is a part of the Northern Adriatic. Marine water for particulate organic matter (POM) was sampled in early and later summer 2008 and in spring 2009. 64 sampling sites (from the town Savudrija in the north to the city of Rijeka in the south) with different amounts of anthropogenic inputs were chosen (**Figure 1**). The marine environment of coastal areas along Istra Peninsula is exposed to and affected by municipal and industrial sewages from cities, marinas and ports and in summer additionaly by tourism (touristic facilities, camps). As comparable areas, anthrophogenically impacted locations in Pirovac Bay and unaffected offshore locations of Koranti Islands were used (Dolenec M. et al., 2011).

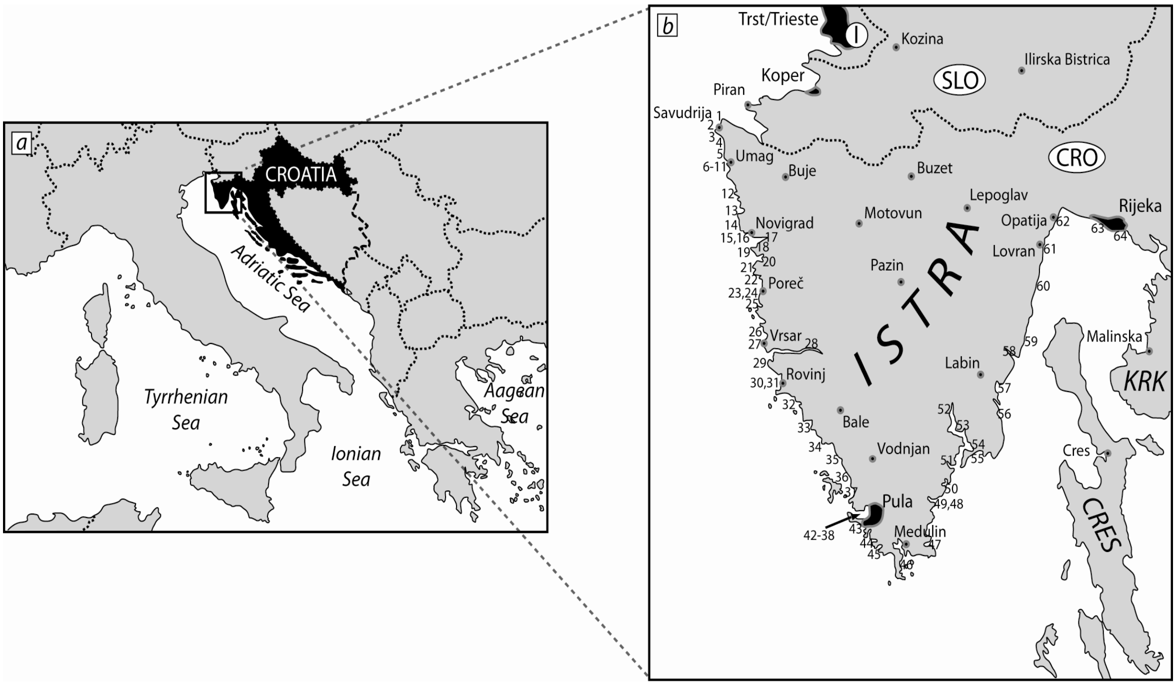

Fig. 1. (a) Position (marked by a box) of the study area in Southern Europe and (b) detailed position of sampling locations along the Istra coast.

Sampling and analysis

Marine water for POM was sampled at about 1 m from the coast at 1 m depth. 10 l of water were filtered through glass microfibre filters (GF/C, Whatman). In the laboratory, filters were dried, catching material were taken from the filters and packed into tin capsules for following isotopic analyses.

The nitrogen isotopic composition was measured using a Europa 20-20 continuous-flow isotope ratio mass spectrometer with an ANCA SL preparation module (PZD Europa

Ltd, UK). The results are expressed in the standard δ^{15}N notation as the relative per mil (‰) difference between the sample and the standard according the following equation:

$$\delta^{15}\mathrm{N} = [R_{\mathrm{sample}}/R_{\mathrm{standard}}-1] \times 1000\ (‰),$$

where R represent the atomic ^{15}N/^{14}N ration in the sample and standard (atmospheric nitrogen, δ^{15}N = 0‰), respectively. The analytical precision (1 standard deviation) of triplicate analyses of IAEA N-1 and N-2 standards was better than ± 0.16 ‰. Precision (1 standard deviation) of duplicate isotope analyses of samples was within ± 0.2 ‰.

Results and discussion

The results of δ^{15}N in POM sampled at three sampling periods along Istra coast are presented in **Table 1**, while **Table 2** snows the basic statistics of the presented results.

Table 1. δ^{15}N values (‰) of particular organic matter (POM) collected at 64 locations along the Istra peninsula coast in summer from summer 2008 to spring 2009.

Sample No.	Sampling site	06,07/2008	Sampling time 08,09/2008	2009	Sample No.	Sampling site	06,07/2008	Sampling time 08,09/2008	2009
1	Savudrija I	5.0	5.5	5.4	33	Bale		5.4	6.1
2	Savudrija II		6.9	4.4	34	Barbariga		6.1	5.3
3	Savudrija III	6.1	6.9		35	Uvala Peroj		6.2	4.4
4	Zambratija I	4.1	7.0	5.5	36	Fažana		5.0	4.7
5	Zambratija II		7.2		37	Štinjan		6.2	6.0
6	Umag I	4.9	5.9	3.4	38	Pula I		0.4	5.4
7	Umag II	5.5	6.6	3.7	39	Pula II		-0.3	
8	Umag III	6.7	6.9	4.1	40	Pula III		1.1	
9	Umag IV	5.8	6.0	4.5	41	Pula IV		-0.6	5.3
10	Umag V		5.2		42	Pula V		-0.8	
11	Umag VI		9.8		43	Stoja		8.1	6.4
12	Lovračica	5.4	6.3	5.2	44	Banjole I		9.2	5.0
13	Reef Flat Dajla	3.7	6.4	5.2	45	Banjole II		4.2	5.5
14	Kostanjija	5.4	6.3	5.3	46	Trumbuja		5.6	3.9
15	Novigrad I	6.1	5.4	5.2	47	Luka Kuje		6.1	3.3
16	Novigrad II	6.5	6.0	3.5	48	Luka Budava I		6.5	4.6
17	Mirna River	4.8	5.4	5.5	49	Luka Budava II		5.5	
18	Tarska Uvala	4.2	4.5	5.2	50	Vinjole			1.7
19	Lanterna-Zub		5.3	4.5	51	Krnična			2.7
20	Červar		4.7	4.0	52	Raša I		5.6	3.9
21	Rt Busuja		4.6	4.7	53	Raša II		13.8	5.9
22	Materada		5.6	5.0	54	Raša III			2.2
23	Poreč I		5.6	3.4	55	Koromačno			3.5
24	Poreč II		6.0	4.4	56	Guboke			1.7
25	Poreč III		5.6	3.7	57	Rabac			2.3
26	Funtana		5.9	3.2	58	Plomin			4.5
27	Vrsar		6.4	4.0	59	Brestova			2.7
28	Limski kanal		5.5	5.4	60	Mošćeniška Draga			1.7
29	Valalta		6.4	4.9	61	Lovran			2.8
30	Rovinj I		5.8	4.4	62	Opatija			2.7
31	Rovinj II		5.3	5.4	63	Rijeka I			2.9
32	Veštar		4.7	4.7	64	Rijeka II			-0.4

$\delta^{15}N$ in POM varied between -0.8 ‰ and +13.8 ‰, with a mean value of 4.9 ‰ (**Table 2**) and show significant $\delta^{15}N$ differences between sampling locations. The prevalent measured $\delta^{15}N$ values are in range from 5.0 to 6.0 ‰ (**Table 1**) and reflect the impact of municipal sewages of bigger cities as well as pollution from local septic systems of the smaller settlements, hotels and camps.

Table 2. Descriptive basic statistics (mean, min, max, SD) of nitrogen isotope composition of particular organic matter (POM) from Istra coast.

	06,07/2008	08,09/2008	2009	All
Mean	4.2	5.3	5.6	4.9
Max	6.4	6.7	13.8	13.8
Min	-0.4	3.7	-0.8	-0.8
SD	1.3	0.9	2.4	1.9

Very low $\delta^{15}N$ values, even negative, were observed in Pula and Rijeka. Such results are explained to be the result of purification plants that remove undesirable materials, chemicals and biological contaminants from municipal and industrial cities sewages. Simultaneously, nitrogen isotope composition in POM at the Pula sampling location shows also higher values, comparable to the contaminated sites. These results can be the consequence of the rapid movement of the POM floating material.

Apart from geographic position, the results show prominent temporal fluctuations within individual sampling sites. Generally, higher $\delta^{15}N$ values were observed at the late summer (August, September 2008) and lower in spring (April 2009) (**Table 1**). Relatively large variations of $\delta^{15}N$ can be explain with the higher amounts of the organic matter in the summer months and also with the movement of floating material owing to the wind, current circulation and tides.

Above-described $\delta^{15}N$ values were compared with the values of POM from locations of different range of anthropogenic input in Central Adriatic; highly affected semi-enclosed Pirovac Bay and unaffected areas around Kornati Island (Dolenec M. et al., 2011) (**Table 3**).

Table 3. Comparison of $\delta^{15}N$ values (‰) of particular organic matter (POM) measured along the Istra peninsula coast with the Pirovac Bay and Kornati Islands.

Location	Mean	Max	Min
Istra coast (our research)	4.9	13.8	-0.8
Pirovac Bay (Dolenec M., et al., 2011)	7.1	8.6	6.1
Kornati Islands (Dolenec M., et al., 2011)	3.2	4	1.8

$\delta^{15}N$ values showed significant differences between observed and comparative sampling sites. Generally, the $\delta^{15}N$ values measured along Istria coast were the same or lower than values from semi-enclosed Pirovac Bay. The latter is one of the most impacted areas in Central Adriatic affected by municipal and industrial sewages from cities and touristic facilities in the summer. An important difference in factors that influence to the POM movement and distribution in water column between the Pirovac Bay and Istra coast areas is also the exposition of the areas to the winds that is perceptibly larger along Istra coast.

The $\delta^{15}N$ values of POM measured in relatively unaffected areas of Kornati Island are obviously lower than in Istra sampling sites and present the natural variability of stable nitrogen isotope composition (reference sites).

Conclusions

We conclude that the stable isotope composition of nitrogen in particulate organic matter (POM) may be used as applicable tracer for detecting human sewage inputs into marine coastal ecosystem.

It was observed that anthropogenically derived organic matter from inadequate municipal infrastructure can cause the increase of $\delta^{15}N$ values in POM and consecutive negatively influence on the coastal marine ecosystem. On the other hand, the purification plants can cause the depletion (even negative) of $\delta^{15}N$ values as was observed in POM samples from Pula and Rijeka cities.

Relatively larger $\delta^{15}N$ values at the end of the summer compare to the spring sampling period can be explain as the result of higher amounts of the organic matter due to tourism and also with the rapid and changeable movement of floating POM material in the water column owing to the wind, current circulation and tides.

The ^{15}N enrichment observed in POM from Istra coast were lower than in anthopogenically more affected semi-enclosed Pirovac Bay and significantly higher than unaffected sampling locations of Koranti Islands.

Acknowledgments

The research was financially supported by the Ministry of Higher Education, Science and Technology, Republic of Slovenia (Bilateral projects between Croatia and Slovenia 2001–2009), Slovenian Research Agency (ARRS) and Geoexp, d.o.o., Tržič, Slovenia.

References

Constanzo, S.D., Donohue, M.J., Dennison, W.C., Loneragan, N.R. & Thomas, M. (2001): A new approach for detecting and mapping sewage impacts. *Marine Pollution Bulletin*, Vol. 42, pp. 149-156.

Dolenec, M., Žvab, P., Mihelčić, G., Lambaša Belak, Ž., Lojen, S., Kniewald, G., Dolenec, T., Rogan Šmuc, N. (2011): Use of stable nitrogen isotope signatures of anthropogenic organic matter in the coastal environment: A case study of the Kosirina Bay (Murter Island, Croatia). *Geologia Croatica*. Vol. 64, No. 2, pp. 143-152.

Dolenec, T., Lojen , S., Kniewald, G., Dolenec, M., Rogan, N. (2006): $\delta^{15}N$ of particulate organic matter and *Anemonia sulcata* as a tracer of sewage effluent transport in the marine costal ecosystem of Pirovac Bay and the Murter Sea (Central Adriatic). *Materials and Geoenvironment*. Vol. 53, No. 1, pp. 1-13.

Dolenec, T., Lojen, S., Kniewald, G., Dolenec, M., Rogan, N. (2007): Nitrogen stable isotope composition as a tracer of fish farming in invertebrates *Aplysina aerophoba*, *Balanus perforatus* and *Anemonia sulcata* in central Adriatic. *Aquaculture*. Vol. 262, pp. 237-249.

Evgenidou, A. & Valiela, I. (2002): Response of Growth and Density of a Population of Geukensia demissa to Land-Derived Nitrogen Loading, in Waquoit Bay, Massachusetts, Estuarine, Coastal and Shelf Science 55, 125-138.

Gaston, T.F., Kostoglidis, A. & Suthers, I.M. (2004): The ^{13}C, ^{15}N and ^{34}S signatures of a rocky reef planktivorous fish indicate different coastal discharges of sewage, Marine and Freshwater Research, 55, 689-699.

Vizzini, S. & Mazzola, A. (2006): The effects of anthropogenic organic matter inputs on stable carbon and nitrogen isotopes in organisms from different trophic levels in a southern Mediterranean coastal area, Science of The Total Environment, 368, 723-731.

CONTENT OF CHALCOPHILE ELEMENTS Cd, Cu, Pb, Zn DERIVED FROM AQUACULTURAL ACTIVITY NEAR VRGADA OF MARINE SEDIMENTS (CENTRAL ADRIATIC, CROATIA)

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Abstract

The paper presents the study of the environmental impact of marine aquaculture on the local ecosystem. For this purpose, the chalcophile element content (Cd, Cu, Pb, Zn) in the marine surface sediment at the fish farm near the Vrgada Island in the Central Adriatic was examined. The results indicate low concentrations of presented elements; average values of Cd 0.11 ppm, Cu 4.96 ppm, Pb 8.33 ppm and Zn 16.58 ppm. Such results suggest that the effect of observed fish farm activity on the local marine ecosystem is practically negligible. Furthermore, calculated geoaccumulation index values indicate that the sediment below the investigated farm is uncontaminated.

Key words: Marine sediment, fish farm, halcophile elements, geoaccumulation index.

Introduction

Among numerous polluting substances, heavy metals present one of the biggest environmental problems due to their toxicity, long time persistence in the contaminated environment and their bioaccumulation in living organisms. The latter has become increasingly significant scientific topic in recent years due to its detrimental effect on the food chain and consecutive for humans.

Sediment elemental concentrations were generally thought to be the result of a variety of processes, including natural factors such as weathering of heterogeneous geology, local seabed morphology and hydrological and chemical status of seawater, as well as anthropogenic input (industrial, mining and urban wastes) (Dolenec et al., 1998). It is expected that also intensive aquaculture activity has the potential to modify natural concentrations of metals in local sediments, with the metal output of farms observed to be up to several tons per day (Tovar et al., 2000). The aquaculture activity can affect the surrounding environment with uneaten feed, faeces, excreted metabolic wastes and medicines (Dean et al., 2007). Many papers have suggested that metal concentrations in sediments have been elevated as a consequence of both the food used in farms and subsequent faecal output (Uotila, 1991; Chou et al., 2002; Belias et al., 2003; Brooks & Mahnken, 2003; Schendel et al., 2004; Smith et al., 2005; Mendiguchía, et al., 2006). Simultaneously, other studies have established at some sites that sediment metal enrichment is negligible (Urdaneta, 1995; Carbonell et al., 1998; Basaran et al., 2010).

Among the geochemical elements, particularly chalcophile elements can be extremely toxic to the environment and also human health (Dauvalter et al., 2009). Therefore, the present study focuses on the concentration of the chalcophile elements Cd, Cu, Pb, and Zn in sediment around fish farm near Vrgada Island.

Study area

The investigated fish farm is positioned south-east of Vrgada Island, which is located off of the central Croatian coast between Zadar and Šibenik in the Murter Sea (Central Adriatic). The farm is situated around 4 nautical miles from the mainland and is surrounded by five islands. The total area under aquaculture covers 10,000 m^2 and extends in a predominantly NW-SE direction. Water depth around the fish cages varies between 20 and 35 m and the predominant direction of water currents is from south-east to north-west, with a mean current velocity of around 6 cm s^{-1} (max 15 cm s^{-1}) and a maximal residual current velocity of 2.5 cm s^{-1}. Geologically, the investigated area and hinterland consist of Cretaceous carbonates (Mamižić, 1966).

Fish-producing activities in the area were established in 1998. The observed farm breeds sea bass (*Dicentrarchus labrax*) and sea bream (*Sparus aurata*), with annual production totalling around 550 t. Fish are kept in polyethylene-polypropylene cages with a diameter between 12 and 22 m, depending on the animals' size and age.

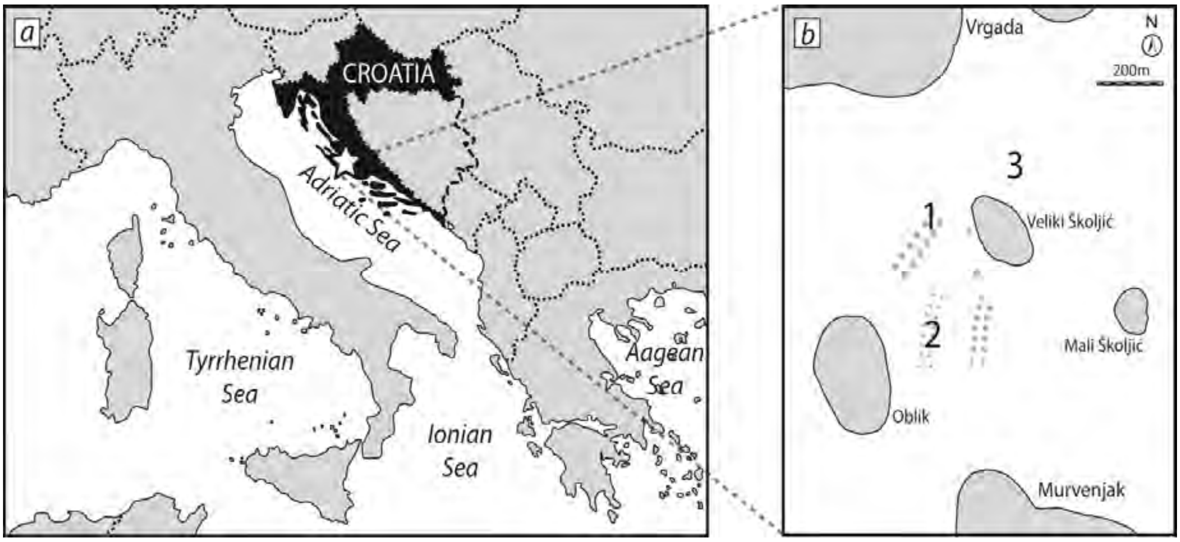

Fig. 1. (a) Position (indicated by a star) of the study area in Southern Europe and (b) detailed position of sampling locations (1, 2, 3) around the fish farm near Vrgada.

Materials and methods

Sampling and analysis

Sediment samples were collected in July 2007 (A) and in two sampling periods (June and August) in 2009 (B,C) at three selected sites located at different distances from the fish cages. The first sampling site was positioned below the cage containing older fish where production was greatest (1A, 1B, 1C), the second was situated below or in close proximity to the cage housing juvenile fish (2A, 2B, 2C), and the third sampling position was located 100 m from (and thus was not directly affected by) the farm and was used as a reference site (3A, 3B, 3C). Samples were collected during scuba dives carried out at a depth of around 20 m, with 10 cm diameter plastic corers sampling to a depth of between 6 and 18 cm, depending on sediment consolidation. After that, sediment cores were stored in a cool box and later frozen. In the laboratory, the sediment cores were sliced every 1 to 2 cm and dried until a constant weight had been reached. Dried sediment samples were homogenized and crushed by grinding in an agate mortar to a fine powder for subsequent analysis.

The geochemical analyses of chalcophile elements (Cd, Cu, Pb and Zn) was obtained at a certified Canadian commercial laboratory (ACMELAB: Acme Analytical Laboratories, Vancouver, Canada) using inductively-coupled plasma mass spectrometry (ICP-MS). The analytical accuracy and precision of the analysis were assessed using an international marine sediment standard MAG-1 (US National Bureau of Standards) as well as duplicate measurements some sediment samples. The analytical precision and accuracy were found to be better than ±5 %.

Basic statistical analyses (mean, min, max, SD) were performed by the statistical software program Statistica 8.0. In order to determine the existence of any association between the elements, a Person multiple correlation analysis was applied. Box-plot diagrams were used to present the spatial distributions.

Geoaccumulation index (I_{geo})

The geoaccumulation index was first devised by Müller (1969) as a method to estimate the degree of metal pollution by comparing current and pre-industrial (unaffected) metal concentrations of sediment. The index is calculated using the following formula:

$$I_{geo} = \log_2 C_n / 1.5 B_n$$

where C_n is the measured concentration of metal (n) in the sample and B_n the geochemical background (reference) level of the metal (n). In our study the reference values B_n used for the investigated heavy metals were: 98 ppm for Cd, 24.7 ppm for Cu, 11 ppm for Pb and 73 ppm for Zn (reverence values were chosen from; surficial sediment from the Central Adriatic for Cu, Pb and Zn; Dolenec et al., 1998 and upper continental crust for Cd; Taylor and McLennan, 1994). The factor of 1.5 is the background correction factor used for lithogenic variation of metals.

Müller (1969) classified I_{geo} values using 7 descriptive classes characterised by varying degrees of enrichment above background values: Class 0 (uncontaminated, $I_{geo}<0$), Class 1 (uncontaminated to moderately contaminated, $0<I_{geo}<1$), Class 2 (moderately contaminated, $1<I_{geo}<2$), Class 3 (moderately to strongly contaminated, $2<I_{geo}<3$), Class 4 (strongly contaminated, $3<I_{geo}<4$), Class 5 (strongly to extremely contaminated, $4<I_{geo}<5$) and Class 6 (extremely contaminated, $I_{geo}>5$).

Results and discussion

The concentrations of chalcophile elements (Cd, Cu, Pb, Zn) in sediment sampled from three different locations at the aquaculture farm near Vrgada were lower at all sampling locations with respect to the mean values of surface sediment from the Central Adriatic (Dolenec et al., 1998) as well as concentrations of upper continental crust for Cd (Taylor & McLennan, 1995) (Table 1).

Concentrations of Cd, Cu, Pb and Zn

Several papers have evaluated heavy metal content of sediment associated with aquacultural activities (Chou et al., 2002; Belias et al., 2003; Mendiguchía et al., 2006; Dean et al., 2007; Sutherland et al., 2007; Basaran et al., 2010; Wu & Yang, 2010). In such studies the most frequently-investigated metals are cadmium, copper, zinc and lead, which are known to be related to either fish food pellets (Zn) or are found in antifouling chemicals used in the treatment of cage nets (Cu) (Basaran et al., 2010). For correlative purpose, the Cd, Cu, Pb and Zn concentrations of sediment samples obtained in the present study will now be discussed and compared in detail with levels found in sediment from other fish farms.

Table 1. Concentrations of chalcoplile elements of sediment samples taken from the studied fish farm near Vrgada (BDL=below detection limit). Basic statistics (mean, min, max and SD) of the sediment samples. Mean elemental concentrations (ppm) of surficial sediments from the [CA]Central Adriatic Sea for Cu, Pb and Zn(Dolenec et al., 1998) and concentrations (ppm) of [UCC] upper continental crust for Cd (Taylor & McLennan, 1995).

Sample	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
1A-1	0.20	8.90	17.00	33.00
1A-2	0.20	2.80	7.70	12.00
1A-3	0.20	6.20	12.10	18.00
1A-4	0.20	7.10	15.60	22.00
1A-5	0.20	9.00	17.40	24.00
1A-6	0.10	10.00	16.70	23.00
1A-7	0.20	9.10	15.30	22.00
1A-8	0.10	8.70	12.90	20.00
1A-9	0.20	7.60	11.60	17.00
1A-10	0.10	7.60	10.60	17.00
2A-1	0.20	1.10	3.70	8.00
2A-2	BDL	1.50	3.30	8.00
2A-3	0.20	1.50	3.50	9.00
2A-4	BDL	1.20	2.40	5.00
2A-5	BDL	2.10	3.60	9.00
3A-1	BDL	1.00	4.70	4.00
3A-2	BDL	1.10	4.50	4.00
1B-1	0.20	7.40	9.40	37.00
1B-2	0.20	7.80	9.70	29.00
1B-3	0.20	7.40	10.40	33.00
1B-4	0.20	7.90	11.80	27.00
1B-5	0.10	7.00	10.80	18.00
1B-6	0.10	9.90	10.50	18.00
1B-7	BDL	6.80	7.90	14.00
1B-8	0.10	7.80	8.10	15.00
1B-9	0.10	7.00	6.10	20.00
2B-1	BDL	3.90	7.60	19.00
2B-2	BDL	1.40	4.00	6.00
2B-3	BDL	2.00	4.90	9.00
2B-4	0.10	3.80	6.20	19.00
2B-5	BDL	3.70	6.80	12.00
2B-6	0.07	3.10	7.40	14.00
3B-1	0.10	6.10	10.30	24.00
3B-2	BDL	5.10	9.90	15.00
3B-3	BDL	6.00	11.20	16.00
1C-1	BDL	1.90	3.50	12.00
1C-2	BDL	1.50	3.10	6.00
1C-3	BDL	1.40	3.30	9.00
1C-4	BDL	1.70	3.70	11.00
1C-5	BDL	2.00	4.10	12.00
1C-6	BDL	1.80	3.60	11.00
1C-7	BDL	1.60	3.90	11.00
2C-1	BDL	2.20	4.60	11.00
2C-2	BDL	4.60	8.00	17.00
2C-3	0.10	6.80	9.30	22.00
2C-4	BDL	6.00	9.30	19.00
3C-1	BDL	8.10	13.30	25.00
3C-2	BDL	4.10	9.00	15.00
3C-3	BDL	7.60	11.60	19.00
3C-4	0.10	6.00	10.40	29.00
Mean	0.110	4.958	8.326	16.580
Min	0.070	1.000	2.400	4.000
Max	0.200	10.000	17.400	37.000
SD	0.055	2.909	4.135	7.848
CA		24.7	11	73
UCC	0.098	25	20	71

As we can se at the Table 2, the concentrations of all four metals in sediment from the fish farm near Vrgada are clearly lower than those observed at Askatos Gulf (Belias et al., 2003), the Bay of Cádiz (Mendiguchía et al., 2006), Loch Craignish (Dean et al., 2007) and from China (Wu & Yang, 2010). Basaran et al. (2010) reported concentrations of copper and zinc in Gulluk Bay, Greece (Cu = 4.39-31.24 ppm, Zn = 2.5-6.7 ppm) that were still at tolerable levels for the local aquatic ecosystem. Concentrations of cooper obtained in the present study are comparable with the lowest values found by Basaran et al. (2010), while zinc values are higher.

Table 2. Mean concentrations (* = maximum concentrations) of chalcophile elements (ppm) in sediment sampled from observed fish farm near Vrgada and other aquaculture activities from the world.

Location	Cd	Cu	Pb	Zn
Vrgada Island, Croatia (our research)	0.11	4.96	8.33	16.58
Askatos Gulf , Greece (Belias et al., 2003)	2.3.1948	31.7-66.9	30.5-41.1	214-679
Bay of Cádiz , Spain (Mendiguchía et al., 2006)		13-27	14-20	40-90
Loch Craignish , Scotland (Dean et al., 2007)		3.5*	805*	921*
China (Wu & Yang, 2010)	0.47	31.56	23.45	41.5
Gulluk Bay, Greece (Basaran et al., 2010)		4.39-31.24		2.5-6.7

Distribution of Cd, Cu, Pb and Zn

Sediment samples were collected at three locations around fish cages during three sampling periods. Te first two locations were positioned in potentially polluted areas, while the third defined as a reference site.

Generally, concentrations of all presented chalcophile elements at the sampling site 1 were greater than at site 2 (**Figure 2**) which is explained with the greater production of excess fish food and faecal matter at the location 1.

However, concentrations in individual sampling periods have shown some deviations. During the first and the second sampling period, the values obtained at site 1A and 1B (below the cage holding older fish) were 1.3 to 4.4-times higher than than at 2A and 2B (**Table 3**).

Table 3. Mean concentrations of chalcophile elements in sediment at separate sampling location (1, 2, 3) in different sampling periods (A, B, C).

Sample	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
1A	0.170	7.700	13.690	20.800
2A	0.122	1.480	3.300	7.800
3A	0.070	1.050	4.600	4.000
1B	0.141	7.667	9.411	23.444
2B	0.075	2.983	6.150	13.167
3B	0.080	5.733	10.467	18.333
1C	0.070	1.700	3.600	10.286
2C	0.078	4.900	7.800	17.250
3C	0.078	6.450	11.075	22.000

In August 2009 an inverse pattern was recorded, with lower concentrations seen below cages holding older (1C) than under those containing smaller (2C) fish (**Table 3**). The lower values observed at site 1C are interpreted to be related to the final late-summer fish catch and consequently lower production.

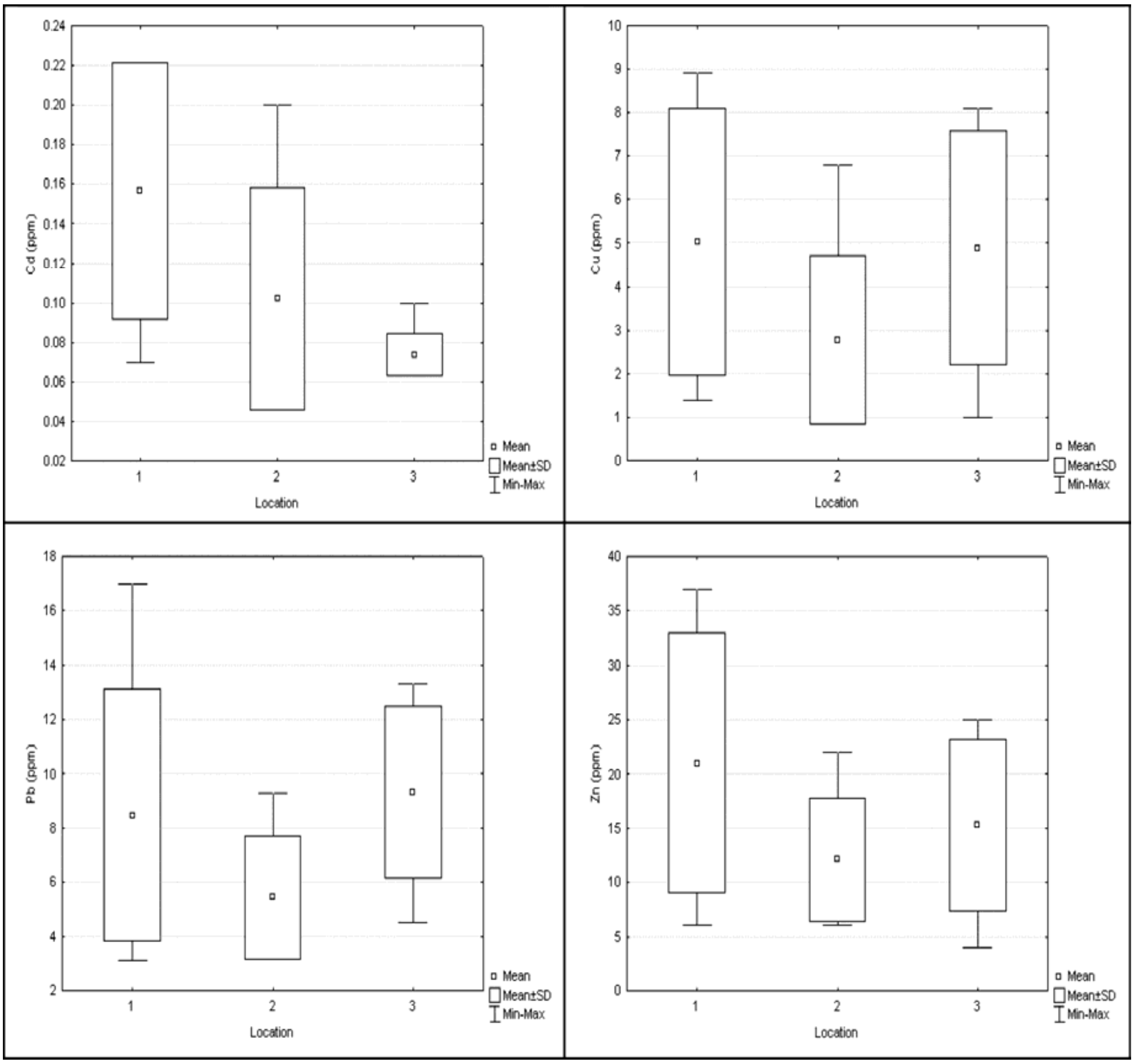

Fig. 2. Box-Plot diagrams of Cd, Cu, Pb and Zn content of sediment samples from three different locations (compiled data from all sampling periods).

Concentrations of Cu, Pb and Zn in sediment at the reference site (3A, 3B, 3C) varied markedly between sampling periods, with the lowest values observed in July 2007 (3A) and the highest in August 2009 (3C) (**Table 3**). This large difference could be interpreted as resulting from slight changes in the location of the reference sampling site. Regarding to the potentially contaminated sites the concentrations at the reference site were the lowest at July 2007 to even the highest at August 2009 (**Table 3**). Levels of Pb in 3C were even higher than the Central Adriatic background value (**Table 3**, Dolenec et al., 1998). Such variable temporal and spatial distribution of values suggests no influence of observed fish farming on underlying sediment.

Geoaccumulation index (I_{geo})

The values of geoaccumulation index for sediment content are shown in **Table 4**.

Table 4. Geoaccumulation index values for sediment sample chalcophile elements content.

Location	Cd	Cu	Pb	Zn
1A	-0.016	0.07	0.219	0.04
2A	-0.018	0.013	0.11	0.028
3A	-0.026	0.004	0.133	0.018
1B	-0.016	0.078	0.2	0.046
2B	-0.026	0.034	0.149	0.032
3B	-0.025	0.068	0.206	0.038
1C	-0.026	0.021	0.112	0.031
2C	-0.025	0.062	0.18	0.038
3C	-0.026	0.073	0.212	0.039

As can be seen, the calculated I_{geo} values were very low, ranging from -0.023 (Cd) to 0.219 (Pb) and are equivalent to Class 0 (uncontaminated). According to these criteria we can asses that sediment around obtained fish farm is unpolluted with chalcophile elements Cd, Cu, Pb and Zn.

Conclusions

According to the presented results we can conclude:

- The concentrations of chalcophile elements (Cd, Cu, Pb and Zn) in sediment around the fish farm near Vrgada were generally below Central Adriatic background values (Dolenec et al., 1998) as well as concentrations of upper continental crust (Taylor & McLennan, 1995).
- The concentrations of Cd, Cu, Pb and Zn were generally below those of other comparable fish-farming areas.
- During the first and second sampling periods, concentrations of chalcophile elements (Cd, Cu, Pb and Zn) in sediment below the cage containing older fish were clearly higher than in sediment sampled below the cage with small fishes. The reason is likely the higher level of production in the former. In August 2009 this trend was reversed, probably associated with the reduction in productivity of the final catch of old fish. The variation of concentrations between sampling periods observed at the reference site can be interpreted as reflecting minor differences between the reference sampling locations chosen.
- The calculated geoaccumulation index (I_{geo}) also show sediment from the selected fish farm to be uncontaminated.

In conclusion, concentrations of heavy metals in sediments near the Vrgada aquaculture farm are generally low, and the influence of such activity on the surrounding marine environment practically negligible.

Acknowledgments

The research was financially supported by the Ministry of Higher Education, Science and Technology, Republic of Slovenia (Bilateral projects between Croatia and Slovenia 2001–2009), Slovenian Research Agency (ARRS) and Geoexp, d.o.o., Tržič, Slovenia.

References

Basaran, A.K., Aksu, M., Egemen, O., 2010. Impacts of the fish farms on the water column nutrient concentrations and accumulation of heavy metals in the sediments in the Eastern Aegean Sea (Turkey). Environ. Monit. Assess. 162, 439-451.

Belias, C.V., Bikas, V.G., Dassenakis, M.J., Scoullos, M.J., 2003. Environmental Impacts of Coastal Aquaculture in Eastern Mediterranean Bays. The case of Asakos Gulf, Greece. Environmental Sciences and Pollution Research. 10, 287-295.

Brooks, K.M., Mahnken, C.V.W., 2003. Interaction of Atlantic salmon in the Pacific Northwest environment III. Accumulation of zinc and cooper. Fisheries Research. 62, 295-305.

Carbonell, G., Ramos, C., Tarzona, J.V., 1998. Metals in shrimp culture areas from the Gulf of Fonseca, Central America. I. Sediments. B. Environ. Contam. Toxicol. 60, 252-259.

Chou, C.L., Haya, K., Paon, L.A., Burridge, L., Moffatt, J.D., 2002. Aquaculture-related trace metals in sediments and lobsters and relevance to environmental monitoring program ratings for near-field effects. Marine Pollution Bulletin. 44, 1259-1268.

Dauvalter, V.A., Kashulin, N.A., Lehto, J. , Jernström, J., 2009. Chalcophile elements Hg, Cd, Pb, As in Lake Umbozero, Murmansk Region, Russia. Int. J. Environ. Res. 3/3, 411-428

Dean , R.J., Shimmield, T.M., Black, K.D., 2007. Cooper, zinc and cadmium in marine cage fish farm sediments: An extensive survey. Environmental Pollution. 145, 84-95.

Dolenec, T., Faganeli, J., Pirc, S., 1998. Major, Minor and Trace Elements in Surficial Sediments from the Open Adriatic Sea: A Regional Geochemical Study. Geologia Croatica. 51/1, 59-73.

Mendiguchía, C., Moreno, C., Mánuel-Vez, M.P., García-Vargas, M., 2006. Preliminary investigations on the enrichment of heavy metals in marine sediemnts originated from intensive aquaculture effluents. Aquaculture. 254, 317-325.

Müller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. Geojournal. 2, 108-118.

Mužimić, P., 1966. Osnovna geološka karta SFRJ 1: 100.000. Tumač za list Šibenik K 33-8. Zvezni geološki zavod Beograd, Beograd.

Schendel, E.K., Nordstrom, S.E., Lavkulich, L.M., 2004. Flock and sediment properties and their environmental distribution from a marine fish farm. Aquac. Res. 35, 483-493.

Smith, J.N., Yeats, P.A., Milligan, T.G., 2005. Sediment geochronologies for fish farm contaminats in Lima Kiln Bay, Bay of Fundy, in: Hargrave, B.T. (Ed.), Environmental effects of marine finfish aquaculture. Springer, Berlin, pp. 221-238.

Sutherland, T.F., Petersen, S.A., Levings, C.D., Martin, A.J., 2007. Distinguishing between natural and aquaculture-derived sediment concentrations of heavy metals in the Broughton Archipelago, British Columbia. Marine Pollution Bulletin. 54, 1451-1460.

Taylor, S.R., McLennan, C.M., 1995. The geochemical evolution of the continental crust. Reviews of Geophysics. 22/2, 241-265.

Tovar, A., Moreno, C., Mánuel-Vez, M.P., García-Vergas, M., 2000. Environmental implications of intensive marine aquaculture in earthen ponds. Marine Pollution Bulletin. 40/11, 984-988.

Uotila, J., 1991. Metal contents and spread of fish farming sludge in southwestern Finland. Marine Aquaculture and Environment. Valtion Painatuskescos Oy, Helsinki,pp. 120-125.

Urdaneta, H., 1995. Contenido total de Cd, Cu, Cr, Mn, Hg, Ni y Pb en sedimentos superficiales de una estación de piscicultura del municipio Páez, Estado Zulia, Venezuela. Bol. Cent. Investig. Biol. 29/1, 1-16.

Wu, X-L., Yang, Y-F., 2010. Accumulation of heavy metals and total phosphorus in intensive aquatic farm sediments: comparison of tilapia *Oreochromis niloticus* x *Oreochromis aureu*, Asian seabass *Lates calcarifer* and white shrimp *Litopenaeus vannamei* farms. Aquaculture Research. 41, 1377-1386.

POLLUTION RELATED WITH ACTIVE MINES IN THE EASTERN MACEDONIA

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Abstract

Within this study, all of the four active metal mines in Eastern Macedonia were studied as potential environmental pollutants with heavy and toxic metals. From the group of the lead-zinc mines were studied Toranica, Zletovo and Sasa while the fourth studied mine was the only mine for copper in Macedonia, the Buchim copper mine. The target groups of this study were airborne dust, water and sediment pollution within the active mines drainage basins. Obtained results confirmed that all the active mines have negative influence to the adjacent environment and that there is pollution of air, water and sediments. Airborne dust pollution around the Toranica mine was up to 25400 mg kg^{-1} Pb, up to 17400 mg kg^{-1} Zn and up to 118 mg kg^{-1} Cd, around the Zletovo mine the values were up to 30900 mg kg^{-1} Pb, up to 67300 mg kg^{-1} Zn and up to 596 mg kg^{-1} Cd, around the Sasa mine the values were up to 14800 mg kg^{-1} Pb, up to 16400 mg kg^{-1} Zn and up to 86 mg kg^{-1} Cd, while around the Buchim mine values were up to 1183 mg kg^{-1} Cu and up to 189 mg kg^{-1} Pb. Water pollution results have shown increased values too. Around the Toranica mine the concentrations were within the range 0.022÷0.187 mg l^{-1}Pb, 0.011÷0.882 mg l^{-1} Zn and up to 0.0055 mg l^{-1} Cd, around the Zletovo mine the concentrations were within the range 0.0095÷6.68 mg l^{-1}Pb, 0.0096÷176 mg l^{-1} Zn and up to 0.146 mg l^{-1} Cd, around the Sasa mine the concentrations were within the range 0.0095÷0.442 mg l^{-1}Pb, 0.022÷12.2 mg l^{-1} Zn and up to 0.06 mg l^{-1} Cd, as well as those around the Buchim copper mine that were within the range 0.004÷509.8 mg l^{-1}Cu, 0.004÷4.89 mg l^{-1} Co and up to 0.3 mg l^{-1} As. Quite similar results were obtained for sediments around the Toranica mine with concentrations within the range 187÷26500 mg kg^{-1}Pb, 1320÷70900 mg kg^{-1} Zn and up to 83 mg kg^{-1} Cd, around the Zletovo mine the concentrations were within the range 1.45÷2113 mg kg^{-1}Pb, 3.34÷1800.2 mg kg^{-1} Zn and up to 17.38 mg kg^{-1} Cd, around the Sasa mine the concentrations were within the range 460÷23500 mg kg^{-1}Pb, 214÷40900 mg kg^{-1} Zn and up to 347 mg kg^{-1} Cd, as well as those around the Buchim copper mine that were within the range 103.33÷99798 mg kg^{-1}Cu, 13.3÷92.47 mg kg^{-1} Co, 3.08÷7.12 mg kg^{-1} Cd and up to 48.37 mg kg^{-1} As.

Key words: lead-zinc mines, copper mine, heavy metals, pollution, toxic metals

Introduction

At the territory of the Republic of Macedonia, during past few decades, actively operate several metallic mines. The most important of them are lead-zinc mines Zletovo, Sasa and Toranica while from the aspect of copper during the last 3 decades is active the Buchim copper mine. Economic and social effects of activity of these mine capacities are clear and significant, but without any doubts are visible their effects to the adjacent environment. Namely, it is familiar that with production of lead-zinc and copper ores is produced solid waste deposited at mine dumps and tailing dams, which has its reflection to the quality of air, surface and ground wasters as well as to soils. As an illustration we would like stress that during the production of 8 decades at Zletovo mine was produced waste, deposited at few cascade dumps, of around 15 Mt, at Sasa around 20 Mt while at Toranica around 3.5 Mt. At the Buchim mine, with an open pit mine operation, during the last 30 years has been produced waste of 140 Mt at the waste dump and 100 Mt at the tailing dam situated above the village of Topolnica. All of these historical wastes has been registered as potential environmental "hot spots" and pose serious source of pollution to the air, water, sediment and soil (Midzic and Silajdzic, 2005; Nordstrom et al., 2000). Part of them were re-cultivated by planting certain species of plants (such an example exists at the Buchim's tailing dam), while the others still produce air pollution.

Positive law regulations allowed partial protection from pollution of those wastes to the environment, but however they still pose serious threats for environmental pollution, because all of them in particular periods experienced accidents (such is the last one when at the beginning of November 2011 the Toranica's tailing dam collapsed). All this was an occasion within the frame of this paper to make a short review of contamination of air, water, sediment and soil around these important mining capacities in Eastern Macedonia.

General features of the active mines in the Macedonia

The subjects of study within this paper are the four active metallic mines Toranica, Zletovo, Sasa and Buchim (Figure 1), where we plan to present some of our latest studies, analyzes and findings.

First of all will be presented the lead-zinc Toranica mine, which has been situated in the NE parts of the Macedonia, close to the Macedonian-Bulgarian border, and it represents one of the youngest and the most modern mines. Its production have started at 1989 and with certain short breaks operates up to date. There are elevated concentrations of Cd, Cu, Mn, Ag, and Bi in the ore, also (Serafimovski et al. 1997). Milling and flotation occurred at the mine and there is a tailings dam below the mine site with a culvert directing the River Toranica beneath the dam.

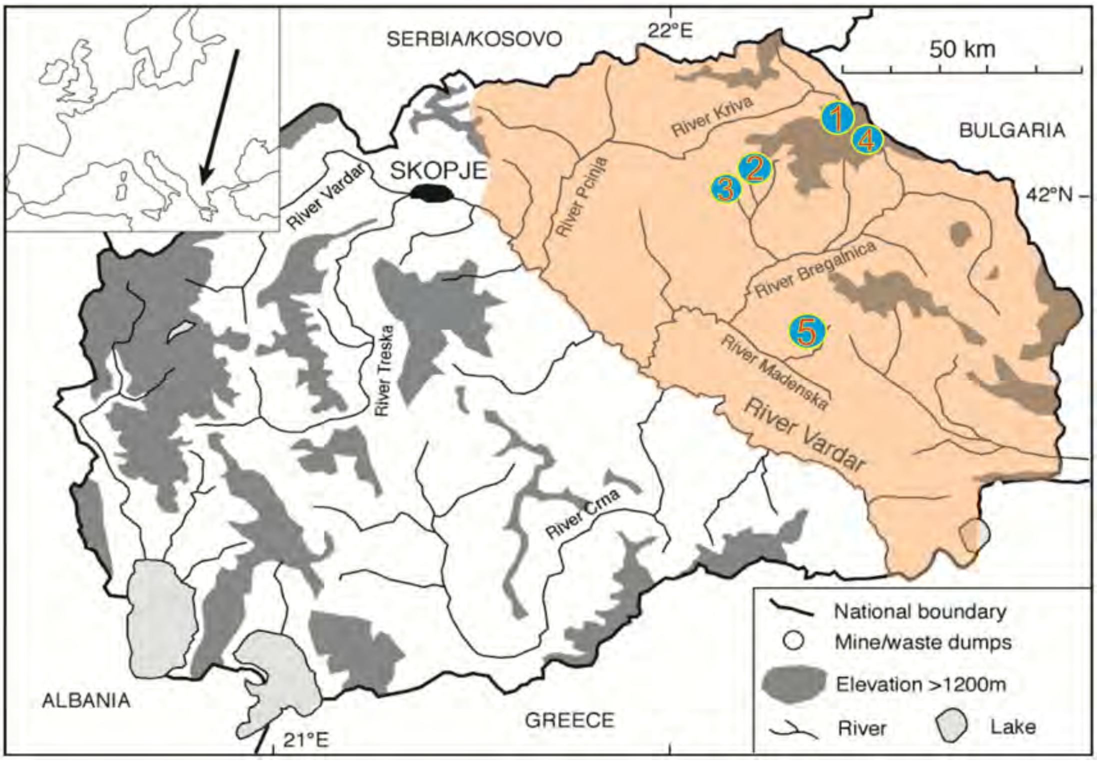


Fig. 1. Map of the Republic of Macedonia showing the major rivers and mining locations used in this study (Alderton et al., 2005; *modified*)
1. Toranica; 2.Zletovo (mine); 3. Zletovo (tailings dam); 4. Sasa; 5. Buchim

Then will follow Zletovo mine, the mine with more than 8 decades tradition of mining production. It is located near the town of Probistip in northeastern Macedonia. The mineralization is related to Tertiary (mostly Miocene) calcalkaline magmatic rocks (dacites and andesites). Ore bodies are located in sub-vertical veins, commonly found sub-parallel to each other and extending for several km in length and to depths of 500 m below surface. The main ore minerals are galena and sphalerite, but tetrahedrite, pyrrhotite, magnetite, chalcopyrite, pyrite, and Mn oxides are also common. Ore grades are 9% Pb and 2% Zn, and significant concentrations of Ag, Bi, Cd, and Cu. Ore is concentrated by flotation at Probistip and tailings were disposed of in two impoundments situated in adjacent valleys. The river Kiselica drains the flotation plant at Probistip and the river Reko drains the area containing the main workings of the Zletovo mine.

After that will follow Sasa mine, as the biggest lead-zinc producing mine with an annual production of more than 750 000 t of ore. It is situated in NE Macedonia, 12 km north of the town of Kamenica and it has been in production since 1962(Aleksandrov et al. 1998; Serafimovski and Aleksandrov 1995). The ore consists of pyrite, galena, and sphalerite, with additional magnetite and chalcopyrite. Ore grades are about 10% Pb + Zn with additional elevated concentrations of Ag, As, Bi, Cd, Mn, and Sb. Ore is concentrated at the mine by flotation, and tailings are stored in a dam in a narrow valley just below the mine. The Kamenica river is culverted beneath the tailings dam and flows 12 km until it meets the Kalimansko reservoir at Kamenica. A major collapse of the culvert in the summer of 2003 allowed 4 Mt of tailings to enter the river and discharge all the way down to the reservoir (Midzic and Silajdzic 2005).

Beside these three lead-zinc producing mines we are going to show a review of the only copper mine in Macedonia, the Buchim mine, which is operated as an open pit mine with an annual production of 4 Mt of ore. It is located in eastern central parts of Macedonia, 10 km west of the town of Radovis. The mine started production in 1980. The deposit is a porphyry copper type deposit (Serafimovski et al. 1996) and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites. The important metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite.The ore consists of 0.3% Cu, 0.3 g/t Au, 1 g/t Ag, 13 g/t Mo. Ore was concentrated by flotation on site and tailings were disposed to a dam in an adjacent valley. The original river is culverted beneath this dam. This river and water from the mine workings combine to form the River Madenska, which joins the River Bregalnica. Standing water in the open pit is a vivid blue-green colour (Alderton et al., 2005).

The major feature of these mines is their production of solid mine waste that introduces significant pollution to the adjacent environs. The intensity of pollution around these facilities is directly related with measures of environmental protection, which recently the best results have shown at the Buchim mine. For all of them the common feature is that their waste dumps and tailing dams are still producing pollution to the air, water and soils around them. Exactly to those threats we are going to concentrate within this paper.

The Toranica Pb-Zn Deposit

Concerning the environmental impact of this mine, we have started our studies with analysis of airborne dust produced during the processes of crushing and grinding of ore (Walton et al., 2003a). During this operation was released significant amount of dust, which may pose serious threats to the environment. Analyzes have shown that heavy metal concentrations in the dust are as those given in Table 1.

Table 1. Analytical data of major heavy metal pollutants in the airborne dust around the crushing and grinding facility at Toranica mine, Macedonia (in mg kg^{-1})

Metal	Measured concetrations	Standard (NOAA)
Arsenic	69.5	5.2
Cadmium	118	3
Copper	681	17
Nickel	48.7	13
Lead	25400	16
Zinc	17400	48

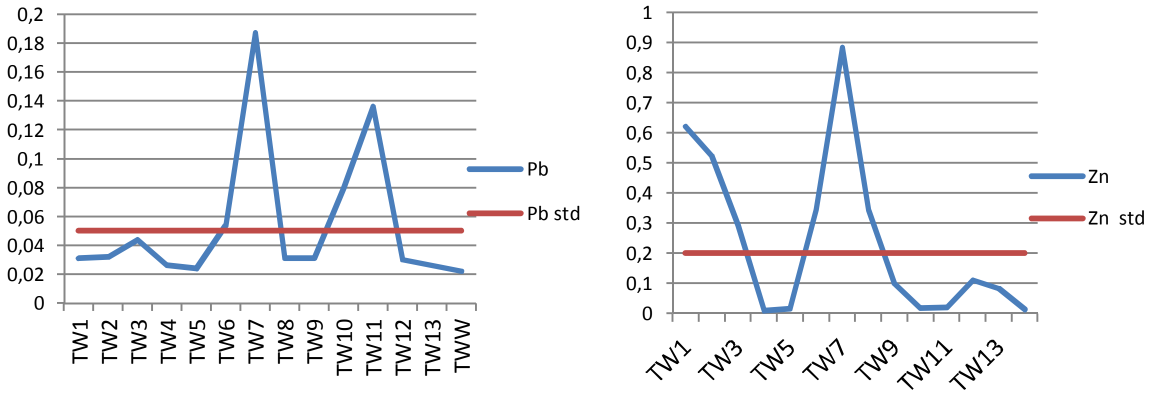
As can be seen from the table above all the measured values multiplexed above the standard values. Enrichment factors ranged from relatively low 3.75 for nickel up to 362.5 for zinc and extreme 1587.5 for lead. Such high levels of concentration of heavy metals introduced by deposition from airborne dust and potential dispersion by wind activity pose very serious threat to the adjacent environment.

Water released from the Toranica mine and around, at first sight looks clean, but however we have proceeded with sampling and analysis at few points. Those results are given in Table 2.

Table 2. Heavy metals concentrations in freshwater samples from the Toranica mine and adjacent areas (mg l^{-1})

Sample	As ($mg\ l^{-1}$)	Cd ($mg\ l^{-1}$)	Ni ($mg\ l^{-1}$)	Pb ($mg\ l^{-1}$)	Zn ($mg\ l^{-1}$)
TW1	0,005	0,0046	0,0055	0,031	0,621
TW2	0,0018	0,0025	0,0031	0,032	0,522
TW3	0,0022	0,0026	0,0019	0,044	0,292
TW4	0,002	0,00025	0,0018	0,026	0,0076
TW5	0,0016	0,00025	0,0019	0,024	0,013
TW6	0,0052	0,0031	0,0016	0,054	0,343
TW7	0,0014	0,014	0,0016	0,187	0,882
TW8	0,0023	0,002	0,0032	0,031	0,341
TW9	0,0021	0,00025	0,0017	0,031	0,099
TW10	0,0044	0,00025	0,0016	0,08	0,017
TW11	0,0019	0,00025	0,0017	0,136	0,019
TW12	0,0016	0,0003	0,0019	0,03	0,109
TW13	0,0016	0,0004	0,0016	0,026	0,083
TWW	0,0029	0,00025	0,0029	0,022	0,011
Stand.	0,05	0,005	0,05	0,05	0,2

From the table above can be seen that the concentration ranges for particular heavy metals were 0.005÷0.052 mg l^{-1} As; 0.002÷0.014 mg l^{-1} Cd; 0.0016÷0.0055 mg l^{-1} Ni; 0.022÷0.187 mg l^{-1} Pb and 0.011÷0.882 mg l^{-1} Zn. As it was expected as the major pollutants in water samples appeared lead and zinc at few points directly related with mining activities (Figure 2).



a *b*

Fig. 2. Concentration of lead *(a)* and zinc *(b)* in freshwater samples within the Toranica drainage system (in mg l^{-1})

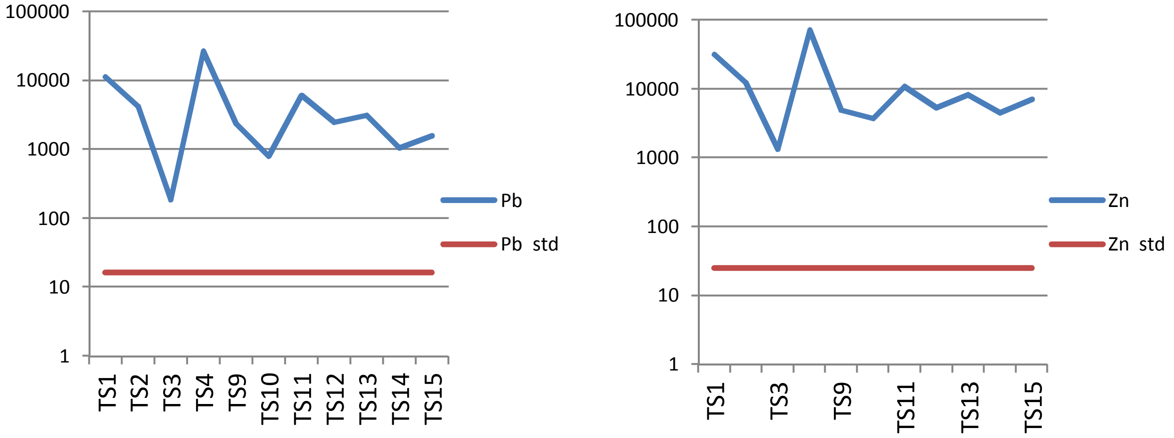
The major influx of lead was at the mine entrance (TW6), pool for final sedimentation (TW7) and collector below the tailing dam (TW11) while the zinc made impact at few more points such as adit entrance (TW1), lake near the adit (TW2), upper flow of the Ruenski stream (TW3) and inflow to the Toranica River (TW8).

Analyses of water samples were complemented by analyses of sediments along the streams in the mine vicinity (Table 3).

Table 3. Heavy metals concentrations in sediment samples around the Toranica mine (in mg kg^{-1})

Sample	As (mg kg^{-1})	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Ni (mg kg^{-1})	Zn (mg kg^{-1})
TS1	111	35	654	11300	43	31900
TS2	25	17	209	4200	8	12200
TS3	21	1,4	12	187	39	1320
TS4	104	83	697	26500	32	70900
TS9	9,7	4,6	29	2360	15	4930
TS10	9,5	2,3	10	794	9,4	3710
TS11	19	10	157	6030	42	10900
TS12	23	5,9	36	2480	27	5310
TS13	30	9,4	39	3130	29	8180
TS14	8	3,5	10	1040	11	4530
TS15	13	4,9	35	1580	17	7090
Stand.	1,1	0,3	17	16	10	25

As can be seen from the table above the ranges of concentrations for were for arsenic from 8 up to 111 mg kg^{-1} As, cadmium from 1.4 up to 83 mg kg^{-1} Cd, copper from 10 up to 697 mg kg^{-1} Cu, lead from 187 up to 26500 mg kg^{-1}, nickel from 8 up to 43 mg kg^{-1} Ni and zinc from 1320 up to 70900 mg kg^{-1} Zn. That all of the measured concentrations were well above the standard values was confirmed with high enrichment factors that were calculated for respective metals. The enrichment factors were from relatively low 2.5 for nickel, 10 for copper and 31 for arsenic, through medium to low 54 for cadmium up to enormous 339 for lead and extreme 585 for zinc. Lead and zinc presence is quite illustrative on the plots concentration versus standard (Figure 3).



a *b*

Fig. 3. Concentration of lead *(a)* and zinc *(b)* in sediment samples within the Toranica drainage system (in mg kg^{-1})
(**Note:** Both plots have logarithmicvertical scales)

The highest values were noticed in sample TS4, sampled from the sediments close to the mine entrance. Also, we would like to stress out that, both lead and zinc, had almost parallel plot trends, which once again confirms they natural association.

Indication of heavy metals pollution to the sediments has been stressed by the calculated geo-accumulation index (Förstner et al., 1993; Lokeshwari and Chandrappa, 2006), which at Toranica's area sediments characterized lead with index range of 2 to 7 (most of them >3) indicating strong to very strong contamination, zinc indexes from 3.5 up to 7.5 (most of them > 4.5) indicating strong to very strong contamination, which have been co-mplemented by calculations for cadmium that have ranged from 1.2 up to 5.2 with majority of values well above 2 indicating without any doubts strong to very strong contamination.

The Zletovo Pb-Zn Deposit

Study of environmental impact of the Zletovo mine was in the same manner as for the previous Toranica mine. Namely, we have started with study of airborne dust produced during the processes of primary crushing of ore, since during this operation is released significant amount of dust, which may pose serious threats to the environment (Walton et al., 2003b). Analyzes have shown that heavy metal concentrations in the dust are as given in Table 4.

Table 4. Analytical data of major heavy metal pollutants in the airborne dust around the primary crushing facility at Zletovo mine, Macedonia (in mg kg^{-1})

Metal	Measured concetrations	Standard (NOAA)
Arsenic	169	5,2
Cadmium	86	3
Copper	354	17
Nickel	10	13
Lead	14800	16
Zinc	16400	48

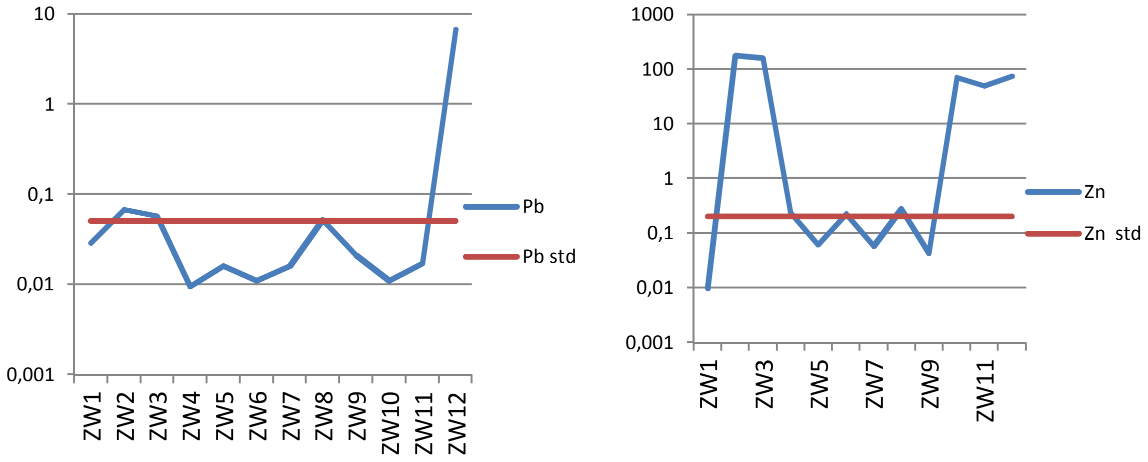
As can be seen from the table above all the measured values multiplexed above the standard values with an exception of nickel. Enrichment factors ranged from mediate ones such were those for copper of 20.8, cadmium of 28.7, arsenic of 32.5 up to high ones for zinc with 341.7 and lead 925. Such high levels of concentration of heavy metals introduced by deposition from airborne dust and potential dispersion by wind activity, pose very serious threat to the adjacent environment.

Water released from the Toranica mine and around, looks clean, but however we have proceeded with sampling and analysis at few points. Those results are given in Table 2.

Table 5. Heavy metals concentrations in freshwater samples from the Zletovo mine and adjacent areas (mg l^{-1})

Sample	As *(mg l^{-1})*	Cd *(mg l^{-1})*	Ni *(mg l^{-1})*	Pb *(mg l^{-1})*	Zn *(mg l^{-1})*
ZW1	0,005	0,00025	0,002	0,029	0,0096
ZW2	0,011	0,402	0,076	0,068	176
ZW3	0,01	0,393	0,072	0,057	160
ZW4	0,014	0,0005	0,0018	0,0095	0,235
ZW5	0,003	0,00022	0,0031	0,016	0,061
ZW6	0,011	0,0003	0,002	0,011	0,22
ZW7	0,0049	0,00026	0,0019	0,016	0,057
ZW8	0,009	0,0017	0,0069	0,052	0,277
ZW9	0,013	0,00023	0,0016	0,021	0,043
ZW10	0,0055	0,146	0,039	0,011	71,2
ZW11	0,0051	0,102	0,031	0,017	49,3
ZW12	0,0062	0,131	0,02	6,68	74,3
Stand.	0,05	0,005	0,05	0,05	0,2

From the table above can be seen that the concentration ranges for particular heavy metals were 0.005÷0.014 mg l^{-1} As; 0.00023÷0.146 mg l^{-1} Cd; 0.0016÷0.076 mg l^{-1} Ni; 0.0095÷6.68 mg l^{-1} Pb and 0.0096÷176 mg l^{-1} Zn. As it was expected, as the major pollutants in water samples at few points directly related with mining and ore processing activities were lead and zinc (Figure 4).



a *b*

Fig. 4. Concentration of lead *(a)* and zinc *(b)* in freshwater samples within the Zletovo drainage system (in mg l^{-1})

(**Note:** Both plots have logarithmicvertical scales)

Lead reached the highest concentrations at four sampled locations, the highest level adit (ZW2), water flow at the mine entrance (ZW3), river culverted under the older tailing dam (ZW8) and pond for deposition of lead (ZW12). Zinc concentrations exceeded maximally allowed concentrations at 8 of 12 sampled locations. Beside those where the lead was increased (ZW2; ZW3, ZW8 and ZW12), zinc was above the limits at Zletovska River near the village (ZW4), Kiselicka River at the tailing dam (ZW6), tunnel exit (ZW10) and water recycling reservoirs (ZW11).

As well as for the Toranica, the water sampling and analyses were complemented by sampling and analyses of sediments from the drainage system within the Zletovo mine area. The results of the analyses are given at Table 6.

Table 6. Heavy metals concentrations in sediment samples around the Zletovo mine (in mg kg^{-1})

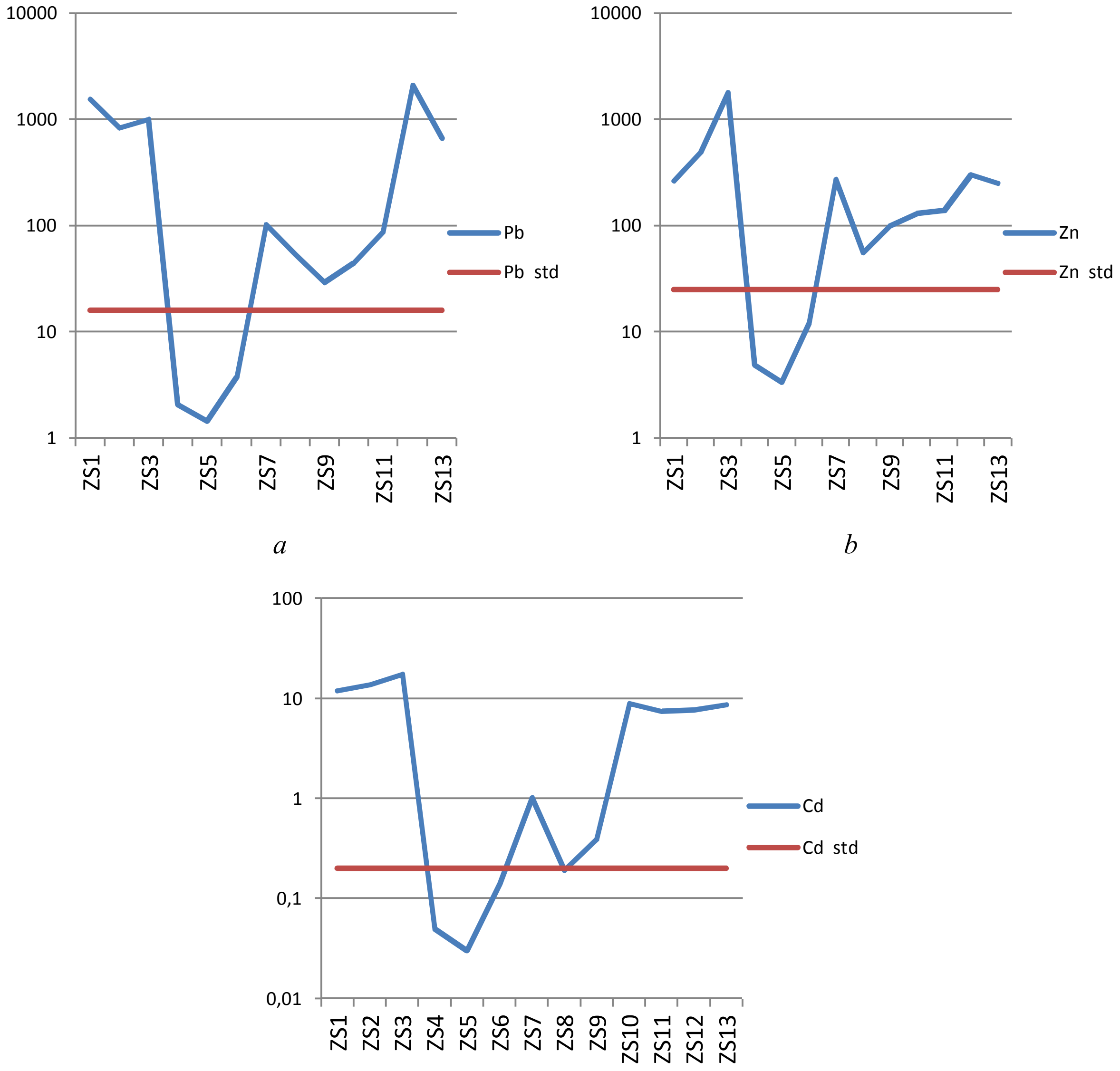
Sample	Fe (mg kg^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})	Cu (mg kg^{-1})	Cd (mg kg^{-1})
ZS1	62500	1010	265,97	1554,7	386,72	11,92
ZS2	49600	1310	494,89	830,02	450,37	13,69
ZS3	53500	1090	1800,23	1008,74	397,69	17,38
ZS4	416	51	4,86	2,06	0,4	0,05
ZS5	251	47	3,34	1,45	0,26	0,03
ZS6	1016	146	12,05	3,76	1,5	0,14
ZS7	1628	747	271,1	102,2	8,92	1,01
ZS8	750	373	55,47	53,78	7,34	0,19
ZS9	710	637	99,11	29,11	4,21	0,39
ZS10	57100	856	130,43	44,34	46,29	8,82
ZS11	47200	1440	139,27	86,93	31,88	7,36
ZS12	48400	803	303,05	2113	49,82	7,56
ZS13	54700	3970	250,03	669,88	40,45	8,66
Stand.	13950	400	25	16	17	0,2

As can be seen from the table above the ranges of concentrations for were for iron from 251 up to 62500 mg kg^{-1} Fe, manganese from 47 up to 3970 mg kg^{-1} Mn, zinc from 3.34 up to 1800.2 mg kg^{-1} Zn, lead from 1.45 up to 2113 mg kg^{-1}, copper from 0.26 up to 450.37 mg kg^{-1} Cu and cadmium from 0.03 up to 17.38 mg kg^{-1} Cd.

That the majority of measured concentrations were well above the standard values was confirmed with high enrichment factors that were calculated for respective metals.

The enrichment factors were from relatively low 2.08 for iron, 2.4 for manganese and 6.5 for copper, median 11.8 for zinc, up to high 29.7 for cadmium and 31.3 for lead. Lead and zinc presence is quite illustrative on the plots concentration versus standard (Figure 5).

The first impression from the plots below is that there is a strong correlation between all the three elements, especially between lead and cadmium, pointing out to a natural association of aforementioned elements. Here the highest values, for all the metals, were determined in the following localities, TrajkovaLivada (ZS1), Livasnica (ZS2), Svinjarnik (ZS3), Zletovica River near the Tripatanci (ZS7), Zletvica River near the Ziganci (ZS9), under the bridge on the road to Dobrevo village (ZS10), near the Kalniste village (ZS11), stream composed of channel draining from the car batteries factory and natural well (ZS12) and under the bridge at the Ratavica village (ZS13). Majority of them are below the mine and mine associated industrial facilities, so the heavy metal pollution can be attributed solely to them.



a *b*

c

Fig. 5. Concentration of lead *(a),* zinc *(b)* and cadmium (*c*) in sediment samples within the Zletovo mine drainage system (in mg kg^{-1})
(**Note:** All the plots have logarithmicvertical scales)

The heavy metals pollution to the sediments at Zletovo vicinity has been re-confirmed once again by the calculated geo-accumulation index, which at Zletovo area sediments characterized the major elements of concern lead, zinc and cadmium that have ranged from 1.3 up to 4.5, from 1 up to 4 and from 1 to 4.1, respectively indicating without any doubts moderate to strong contamination.

The Sasa Pb-Zn Deposit

The last but not least important in the series of study of lead-zinc mines was the Sasa mine. Study of its environmental impact was in the same manner as for the previous Toranica and Zletovo mines.

First of all we started with the study of airborne dust produced during the processes of primary and secondary crushing of ore, since during these operationsare released significant amounts of dust, which can lead to serious threats to the environment (Walton et al., 2003c). Analyzes of heavy metal concentrations in the dust are given in Table 7.

Table 7. Analytical data of major heavy metal pollutants in the airborne dust around the primary crushing facility at Sasa mine, Macedonia (in mg kg^{-1})

Metal	**Measur.conc.** *Primary crushing*	**Measur.conc.** *Secondary crushing*	**Standard (NOAA)**
Arsenic	68.3	95.2	5,2
Cadmium	160	596	3
Copper	811	1200	17
Manganese	3750	4260	330
Lead	30900	7560	16
Zinc	18400	67300	48

As can be seen from the table above all the measured values multiplexed above the standard values with an exception of nickel. Enrichment factors ranged from low ones such were those manganese of 12.14 and arsenic of 15.72, median for copper of 59.15, high for cadmium of 126 and extremely high for zinc with 892.7 and lead 1201.9.

Such high levels of concentration of heavy metals introduced by deposition from airborne dust and potential dispersion by wind activity, without any doubts pose very serious threat to the adjacent environment.

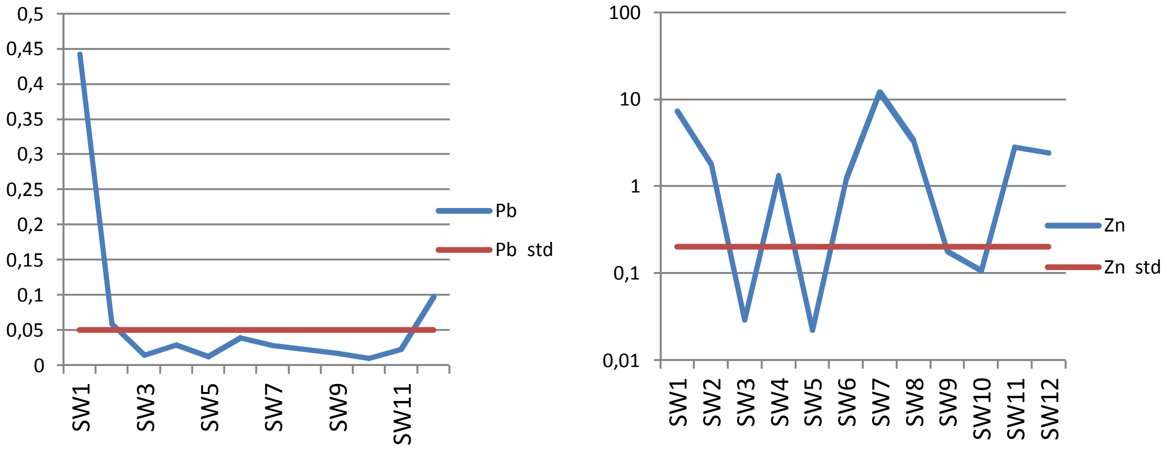
Within this study, as we previously mentioned, we have followed the sampling and analysis programme as for previous two lead-zinc mine. So, in that manner we have sampled and analyzed waters released from the Sasa mine and its adjacent vicinity. The results of our scientific efforts are given in Table 8.

Table 8. Heavy metals concentrations in freshwater samples from the Sasa mine and adjacent areas (in mg l^{-1})

Sample	**As** ($mg\ l^{-1}$)	**Cd** ($mg\ l^{-1}$)	**Cu** ($mg\ l^{-1}$)	**Pb** ($mg\ l^{-1}$)	**Ni** ($mg\ l^{-1}$)	**Zn** ($mg\ l^{-1}$)
SW1	0.0018	0.052	0.518	0.442	0.062	7.36
SW2	0.0058	0.013	0.0018	0.059	0.016	1.8
SW3	0.0017	0.0001	0.0016	0.014	0.0018	0.029
SW4	0.0021	0.0098	0.0088	0.029	0.01	1.33
SW5	0.0034	0.0002	0.0022	0.013	0.0017	0.022
SW6	0.0124	0.0073	0.0013	0.039	0.0077	1.23
SW7	0.0081	0.06	0.012	0.028	0.071	12.2
SW8	0.0027	0.018	0.0021	0.023	0.02	3.38
SW9	0.0054	0.001	0.0023	0.017	0.0018	0.177
SW10	0.0018	0.0004	0.0023	0.0095	0.0017	0.107
SW11	0.0026	0.015	0.0018	0.023	0.017	2.81
SW12	0.0039	0.014	0.0016	0.097	0.015	2.42
Stand.	0.05	0.005	0.05	0.05	0.05	0.2

From the table above can be seen that the concentration ranges for certain heavy metals were 0.0017÷0.0124 mg l^{-1} As; 0.0001÷0.06 mg l^{-1} Cd; 0.0013÷0.518 mg l^{-1} Cu;

0.0095÷0.442 mg l^{-1} Pb, 0.0017÷0.071 mg l^{-1} Ni and 0.022÷12.2 mg l^{-1} Zn. As it was expected, as the major pollutant in water samples at few points directly related with mining and ore processing activities appeared zinc and cadmium while lead levels were rarely above the allowed levels (Figure 6).



a *b*

Fig. 6. Concentration of lead *(a)* and zinc *(b)* in freshwater samples within the Sasa drainage system (in mg l^{-1})
(**Note:** Plot *b)* have logarithmic vertical scale)

Lead reached the highest concentrations at three sampled locations, the downstream from the highest horizontal tunnel at Svinja Reka (SW1), horizontal shaft 15 (SW2) and along the Sasa river 4 km downstream. Zinc concentrations itself exceeded maximally allowed concentrations at 8 of 12 sampled locations. The most common pollutants have not shown some particular correlation.

The water sampling and analyses for this mine were complemented by sampling and analyses of sediments from the drainage system within the Sasa mine area. The results of the analyses are given at Table 9.

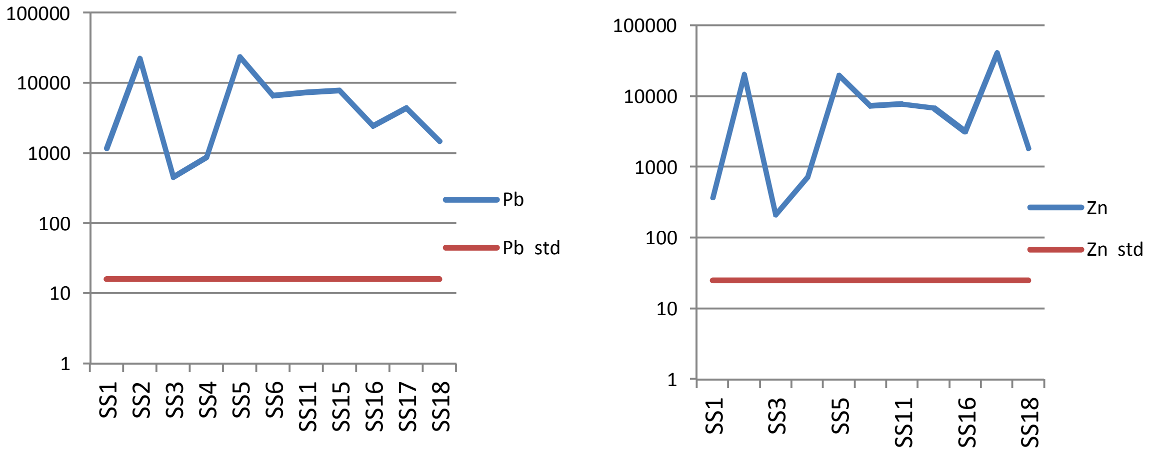
Table 9. Heavy metals concentrations in sediment samples around the Sasa mine (in mg kg^{-1})

Sample	**As** (mg kg^{-1})	**Cd** (mg kg^{-1})	**Cu** (mg kg^{-1})	**Pb** (mg kg^{-1})	**Ni** (mg kg^{-1})	**Zn** (mg kg^{-1})
SS1	58	2.3	126	1170	47	370
SS2	53	177	714	22200	97	20300
SS3	23	2.3	87	460	43	214
SS4	22	5.5	183	879	39	724
SS5	91	155	1210	23500	65	19800
SS6	196	49	538	6570	62	7320
SS11	71	58	1060	7240	41	7800
SS15	895	41	277	7750	51	6800
SS16	78	18	120	2450	47	3140
SS17	419	347	1960	4380	52	40900
SS18	40	6.3	57	1480	44	1860
Stand.	1.1	0.3	17	16	10	25

From the table above can be seen that the ranges of concentrations for heavy metals were various. Namely they were for arsenic from 22 up to 895 mg kg^{-1} As, cadmium from 2.3 up to 347 mg kg^{-1} Cd, copper from 57 up to 1960 mg kg^{-1} Cu, lead from 460 up to 23500 mg kg^{-1} Pb, nickel from 37 up to 97 mg kg^{-1} Ni and zinc from 214 up to 40900 mg kg^{-1} Zn.

That the majority of measured concentrations were well above the standard values was confirmed with high enrichment factors that were calculated for respective metals.

The enrichment factors were from relatively low 5.35 for nickel, low to medium for copper with 33.9 and arsenic with 160.8 and high value enrichment factors for cadmium, zinc and lead with 261.1, 397.2 and 443, respectively. Lead and zinc presence is quite illustrative on the plots concentration versus standard (Figure 7).



a *b*

Fig. 7. Concentration of lead *(a)* and zinc *(b)* in sediment samples within the Sasa mine drainage system (in mg kg^{-1})
(**Note:** Both plots have logarithmic vertical scales)

The strong correlation between lead and zinc was indicated by contours of concentration lines. Both the lines are almost parallel, which strongly supports aforementioned correlaton. The heavy metals pollution to the sediments has been re-confirmed once again by the calculated geo-accumulation index (Förstner et al., 1993; Lokeshwari and Chandrappa, 2006), which at Sasa area sediments characterized arsenic with index range of 2.6 to 6.3 (most of them >3) indicating strong to very strong contamination, cadmium indexes from 1.6 up to 6.6 (most of them >3) indicating strong to very strong contamination. The major elements of concern lead and zinc have ranged from 3 up to 6.9 and from 1.8 up to 7, respectively indicating without any doubts strong to very strong contamination.

The Buchim Cu Deposit

The only one active copper mine within the Macedonia joined the lead-zinc mines in our study of their environmental impact. We have followed the sampling and analysis programme as for lead-zinc mines.

Considering airborne dust pollution we would like to stress out that the study on this subject already exists (Balabanova et al., 2011a), so we used it as representative one. Namely, the median values for Cu in samples of deposited dust taken from the Radoviš area is 396 mg kg^{-1} and the ranges (from 94.8 to 1171 mg kg^{-1}, with high variation in monthly values) for the Topolnica village (the village near the tailing dam) the median values in samples of deposited dust is 150 mg kg^{-1} with ranges (from 52.5 to 1183 mg kg^{-1}) and for the Bučim village (the village located on the boundary to the Buchim open pit mine) the median values in deposited dust samples is 145 mg kg^{-1} and the ranges from 85.3 to 317 mg kg^{-1}. From these results can be seen that the maximum value for the content of Cu was obtained from Topolnica village (settlement near by the flotation tailings landfill). Similar results were obtained for the content of Pb. Previously investigations separated Cu and Pb as anthropogenic introduced elements in the study area (Balabanova et al., 2009; 2010; 2011b; Stafilov et al, 2010). Maximum value for Pb was obtained from the town of Radoviš (189 mg kg^{-1}). Variability in monthly values for lead contents is due to the fact that higher contents of this anthropogenic element are continuously introduced in air with traffic and industry characteristic for the town. Despite the large amounts of total deposited dust from Bučim village, high values for the Pb content were not found

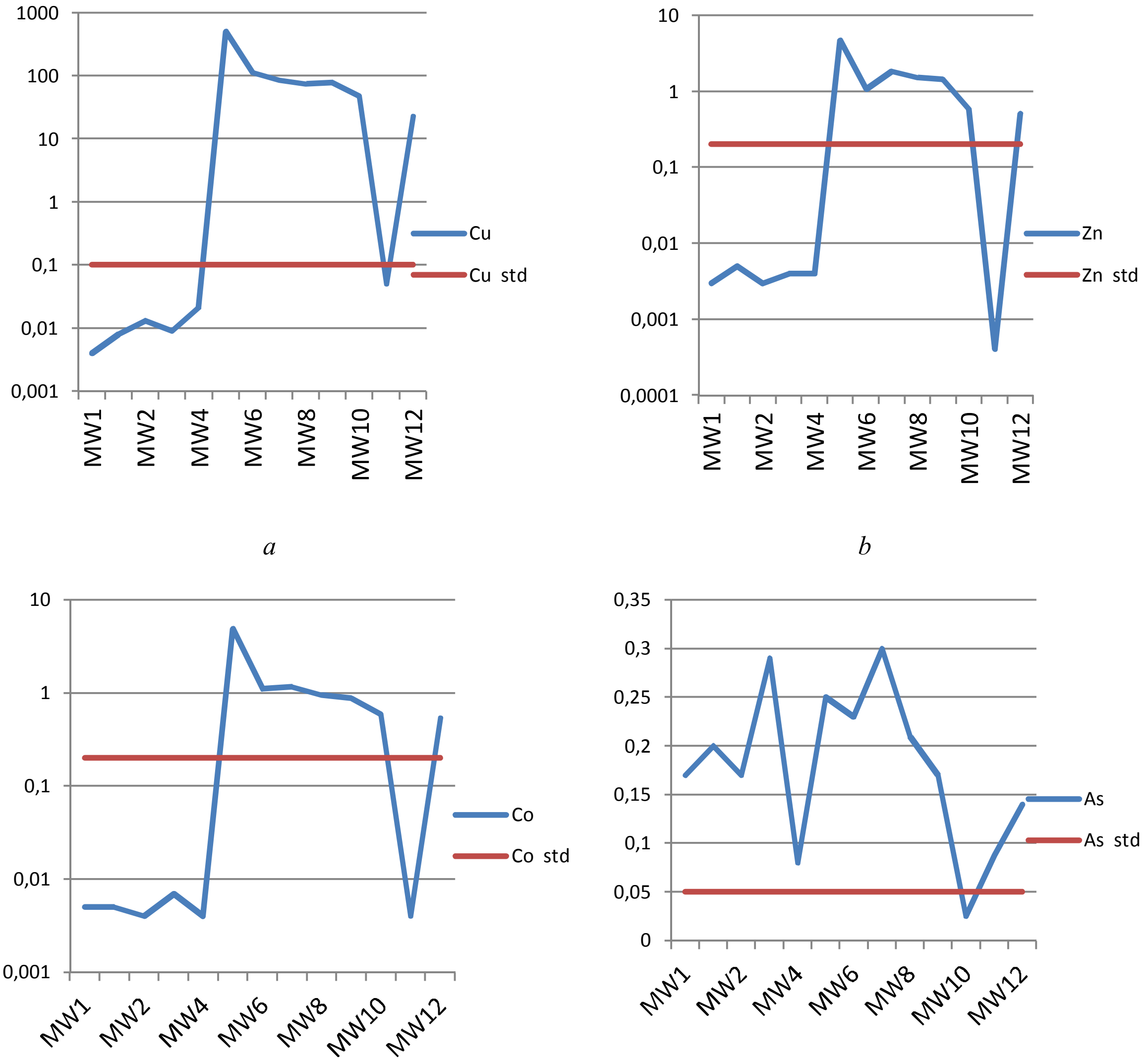
In regards of water pollution around the Buchim mine we have sampled and analyzed waters released from the mine and its adjacent vicinity. The results of our scientific efforts are given in Table 10.

Table 10. Heavy metals concentrations in freshwater samples from the adjacent vicinity of the Buchim mine (in mg l^{-1})

Sample	**Fe** *(mg l^{-1})*	**Zn** *(mg l^{-1})*	**Ni** *(mg l^{-1})*	**Pb** *(mg l^{-1})*	**Cu** *(mg l^{-1})*	**Co** *(mg l^{-1})*	**As** *(mg l^{-1})*
MW1	0.053	0.003	0.003	0.002	0.004	0.005	0.17
MW1'	0.074	0.005	0.006	0.004	0.008	0.005	0.2
MW2	0.035	0.003	0.002	0.001	0.013	0.004	0.17
MW3	0.058	0.004	0.004	0.004	0.009	0.007	0.29
MW4	0.05	0.004	2.57	0.014	0.021	0.004	0.08
MW5	0.023	4.75	0.52	0.025	509.8	4.89	0.25
MW6	0.121	1.08	0.72	0.004	112.5	1.11	0.23
MW7	0.134	1.84	0.53	0.009	85.35	1.17	0.3
MW8	0.179	1.52	0.59	0.005	74.47	0.94	0.21
MW9	0.175	1.44	0.38	0.015	77.22	0.88	0.17
MW10	0.02	0.58	0.004	0.012	47.21	0.59	0.025
MW11	0.025	0.0004	0.32	0.011	0.05	0.004	0.088
MW12	0.017	0.51	0.458	0.008	22.83	0.54	0.14
Stand.	0.5	0.2	0.05	0.05	0.05	0.2	0.05

From the table above can be seen that the concentration ranges for certain heavy metals were 0.017÷0.179 mg l^{-1} Fe; 0.0004÷4.75 mg l^{-1} Zn; 0.002÷2.57 mg l^{-1} Ni; 0.001÷0.025 mg l^{-1} Pb, 0.004÷509.8 mg l^{-1} Cu, 0.004÷4.89 mg l^{-1} Co and 0.025÷0.3 mg l^{-1} As. As it was expected, as the major pollutant in water samples at few points directly related with mining and ore processing activities appeared copper, cobalt, arsenic and zinc (Figure 8), while other elements levels were rarely above the allowed levels.

This situation almost ideally overlapped the theory that the mobility of the heavy metals should be in the following order: Cd>Mo>Sb>Zn>Cu>As>Pb>Ni>Ag (Rogan Šmuc, 2010)



a *b*

c *d*

Fig. 8. Concentration of lead *(a)* and zinc *(b)* in freshwater samples within the Buchim drainage system (in mg l^{-1})
(**Note:** Plots *a), b)* and *c)* have logarithmic vertical scales

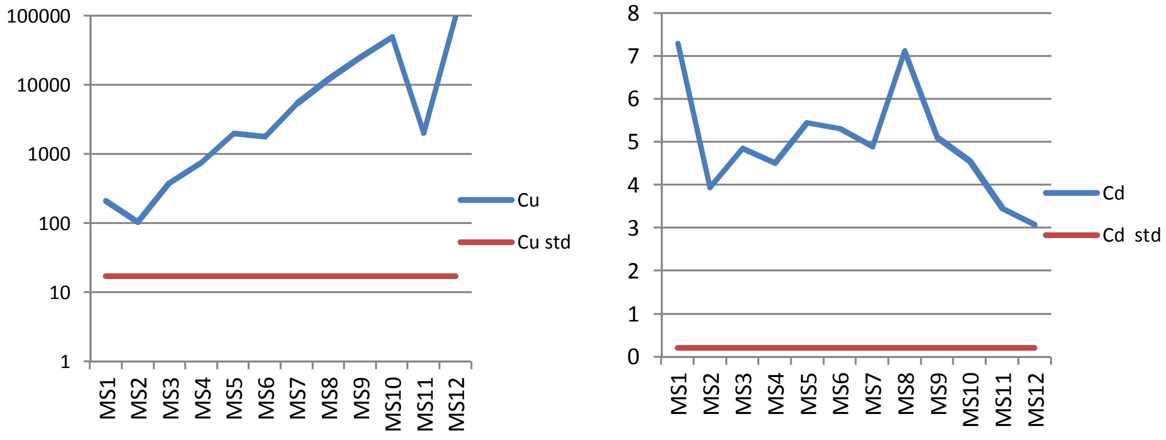
Concentration lines for copper, zinc and cobalt are almost identical suggesting their strong correlation as well as their natural association (Jung, 2001). As the elemental concentration lines suggests the pollution is almost exclusively related with mine or mine related operations.

Even here, with the copper mine, we haven't left the good practice to complement the water sampling and analyses for this mine were complemented by sampling and analyses of sediments from the drainage system within the Sasa mine area. The results of the analyses are given at Table 11.

Table 11. Heavy metals concentrations in sediment samples around the Buchim mine (in % and mg kg^{-1}, respectively)

Sample	Al (%)	Fe (%)	Mn (%)	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})	Co (mg kg^{-1})	Cd (mg kg^{-1})	As (mg kg^{-1})
MS1	1.12	5.45	0.051	211.9	22.24	43.05	15.57	25.13	7.3	47.48
MS2	1.52	2.91	0.047	103.33	15.75	47.75	10.97	13.3	3.94	1.25
MS3	1.78	3.55	0.075	381.32	20.35	53.59	17.59	15.25	4.85	4.41
MS4	1.58	3.3	0.094	755.53	19.51	50.94	18.21	14.95	4.51	2.85
MS5	3.71	4.05	0.049	1957	25.07	55.33	39.85	15.4	5.44	4.47
MS6	2.38	3.98	0.058	1750	18.33	53	18.57	15.84	5.31	3.13
MS7	2.15	3.52	0.055	5299	23.19	58.07	54.27	21.49	4.9	5.72
MS8	2.23	5.42	0.155	12158	49.97	90.92	40.2	58.45	7.12	48.37
MS9	3.57	5.23	0.289	25018	95.83	133.54	38.52	58.02	5.1	11.03
MS10	5.04	3.3	0.142	48835	81.79	279.85	35.05	57.58	4.55	9.57
MS11	2.59	14.54	0.089	2014	102.12	75.55	23.93	19.09	3.45	3.78
MS12	9.98	2.21	0.132	99798	115.25	552.97	35.59	92.47	3.08	5.51
Stand.	0.25	1.4	0.04	17	10	25	16	10	0.2	1.1

From the table above can be seen that ranges of concentrations for heavy metals were various, but without exceptions they all were well above the maximal allowed values. Particular concentration ranges were for alumina from 1.12 up to 9.98 % Al, iron from 2.21 up to 14.54 % Fe, manganese from 0.047 up to 0.289 mg kg^{-1} Mn, copper from 103.33 up to amazing 99798 mg kg^{-1} Cu, nickel from 15.75 up to 115.25 mg kg^{-1} Ni, zinc from 43.05 up to 552.97 mg kg^{-1} Zn, lead from 10.97 up to 54.27 mg kg^{-1} Pb, cobalt from 13.3 up to 92.47 mg kg^{-1} Co, cadmium from 3.08 up to 7.12 mg kg^{-1} Cd and arsenic from 1.25 up to 48.37 mg kg^{-1} As. That all the measured concentrations were well above the standard values was confirmed with high enrichment factors that were calculated for respective metals. Namely, the enrichment factors were from relatively low 2 for lead, 2.6 for manganese, 3 for cobalt, 3.4 for iron, 5 for zinc and nickel, 11 for arsenic, 12.6 for alumina, 25 for cadmium and extremely high 972 for copper. Copper and cadmium expressed concentrations as the most representative are given on the plots at Figure 9.



a *b*

Fig. 9. Concentration of copper *(a)* and cadmium *(b)* in sediment samples within the adjacent area of the Buchim mine (in mg kg^{-1})
(**Note:** Plot *(a)* has logarithmic vertical scale)

The intensity of the heavy metals pollution to the sediments has been confirmed once again by the calculated geo-accumulation index (Förstner et al., 1993), which in this case have ranged from 1.5 up to 8.3 for copper indicating strong to very strong contamination intensity (with majority of values well above index 4 strong-very strong). In this direction similarly behaved cadmium with geo-accumulation index values within the range of 2.3 to 3.2 indicating moderate to strong contamination intensity, as well as arsenic with geo-accumulation index within the range from 1.9 to 3.4 indicating similar contamination intensity to that of cadmium.

Conclusion

Lead-zinc mines in Eastern Macedonia have tradition of mining production of more than 8 decades and during that period have produced solid waste, which directly affects the environment, contaminating at different levels the air, water, sediments and soil. The current study have confirmed that airborne dust pollution around the Toranica mine was up to 25400 mg kg^{-1} Pb, up to 17400 mg kg^{-1} Zn and up to 118 mg kg^{-1} Cd, around the Zletovo mine the values were up to 30900 mg kg^{-1} Pb, up to 67300 mg kg^{-1} Zn and up to 596 mg kg^{-1} Cd while around the Sasa mine the values were up to 14800 mg kg^{-1} Pb, up to 16400 mg kg^{-1} Zn and up to 86 mg kg^{-1} Cd.

Water pollution results have shown increased values too. Around the Toranica mine the concentrations were up to 0.187 mg l^{-1}Pb, up to 0.882 mg l^{-1} Zn and up to 0.0055 mg l^{-1} Cd, around the Zletovo mine up to 6.68 mg l^{-1}Pb, up to 176 mg l^{-1} Zn and up to 0.146 mg l^{-1} Cd while around the Sasa mine they were up to 0.442 mg l^{-1}Pb, up to 12.2 mg l^{-1} Zn and up to 0.06 mg l^{-1} Cd.

Quite similar results were obtained for sediments around the Toranica mine with concentrations up to 26500 mg kg^{-1}Pb, up to 70900 mg kg^{-1} Zn and up to 83 mg kg^{-1} Cd, around the Zletovo mine they up to 2113 mg kg^{-1}Pb, up to 1800.2 mg kg^{-1} Zn and up to 17.38 mg kg^{-1} Cd, while around the Sasa mine they were up to 23500 mg kg^{-1}Pb, up to 40900 mg kg^{-1} Zn and up to 347 mg kg^{-1} Cd.

Production of copper ores at the territory of the Republic of Macedonia have a continuity of more than 30 years. At the Buchim mine during that period of time has been produced solid waste at the waste dump of around 140 Mt while at the tailing dam has been deposited 120 Mt of material. These two "hot spots" have direct and prolongated influence to the adjacent environment causing pollution to air, water and sediment as well as to soils. Namely, airborne dust pollution around the Buchim mine values were up to 1183 mg kg^{-1} Cu and up to 189 mg kg^{-1} Pb. Water pollution results around the Buchim copper mine were up to 509.8 mg l^{-1}Cu, up to 4.89 mg l^{-1} Co and up to 0.3 mg l^{-1} As. Quite similar results were obtained for sediments with up to extremely high 99798 mg kg^{-1}Cu, up to 92.47 mg kg^{-1} Co, 7.12 mg kg^{-1} Cd and up to 48.37 mg kg^{-1} As. These parameters today are changed significantly, namely during last and this year Buchim mine have constructed installation for copper leaching, which includes closed system that receives all surface drainage waters in the adjacent vicinity of the mine. In this manner the negative effects produced by the mining processes were significantly decreased.

References

Alderton, D. H. M., Serafimovski, T., Mullen, B., Fairall, K., James, S., 2005: The Chemistry of Waters Associated with Metal Mining in Macedonia. Mine Water and Environment (2005) 24: 139-149. IMWA Springer Verlag 2005.

Aleksandrov, M., Serafimovski, T. and M'nkov, S., 1998. Silver bearing contents and mode of occurrence of silver in the SasaPb-Zn deposit, eastern Macedonia. GeologicaMacedonica 12: 23-36.

Balabanova, B., Stafilov, T., Bačeva, K., Šajn, R. (2009). Atmospheric pollution with copper around the copper mine and flotation, Bučim, Republic of Macedonia, using biomonitoring moss and lichen technique, *Geologica Macedonica*, 23, 35–41.

Balabanova, B., Stafilov, T., Bačeva, K., Šajn, R. (2010). Bıomonıtorıng of atmospherıc pollutıon wıth heavy metals ın the copper mıne vıcınıty located near Radovıš, Republıc of Macedonıa, *Journal of Environmental Science and Health, Part A, Toxic/Hazardous Substance & Environmental Engineering*, 45, 1504–1518.

Balabanova, B., Stafilov, T., Šajn, R. and Bačeva, K., 2011a. Monitoring deposition of anthropogenic introduced elements in air. case study: copper mine environ. 2nd International Workshop on the UNESCO-IGCP Project: *"Anthropogenic effects on the human environment in the Neogene basins in the SE Europe"* 6-7th October 2011, Zagreb-Croatia, pp. 67-72

Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K. (2011b). Distribution of chemical elements in attic dust as reflection of lithology and anthropogenic influence in the vicinity of copper mine and flotation, *Archives of Environmental Contamination and Toxicology*, 61, 173–184

Förstner, U., Ahlf, W. and Calmano, W., 1993. Sediment quality objectives and criteria development in Germany, *Water Sci. Technol*., **28**, 307

Midzic, S. and Silajdzic, I., 2005. Macedonia. In: Wolkersdorfer C, Bowell R [Eds], Contemporary reviews of mine water studies in Europe, Part 2. Mine Water Environ 24 (1): 21-23

Nordstrom, D. K., Alpers,C. N., Ptacek, C. J., Blowes, D. W., 2000.Negative pH and Extremely Acidic Mine Waters from Iron Mountain, California. *Environmental Science & Technology* 34 (2): 254-258. doi:10.1021/es990646v

Rogan Šmuc, N. (2010). Heavy metal contamination of soils and crops in tertiary basins: A case study of Kočani Field (Macedonia). Dr. thesis, 108 pp.

Serafimovski, T., Cifliganec, V., Jankovic, S. and Boev, B., 1996. Genetic model of the Buchim porphyry copper deposit, Republic of Macedonia. Proc, UNESCO-IGCP project 356, Plate Tectonics of the Alpine metallogeny in the Carpatho-Balkan region, Vol 1, Sofia, p 63-74.

Serafimovski, T., Spasovski, O. and Stankovski, R., 1997. Content and distribution of some elements in the major minerals from the Toranica Pb-Zn deposit (NE Macedonia). Geologica Macedonica 11: 1-15

Jung, M. C. (2001). Heavy metal contamination of soils and waters in and around the Imcheon Au-Ag mine, Korea. Applied Geochemistry, 16, 1369–1375.

Lokeshwari, H. and Chandrappa, G.T., 2006. Heavy Metals Content in Water, Water Hyacinth and Sediments of Lalbagh Tank, Bangalore (India)JOURNAL OF ENVIRON. SCIENCE AND ENGG. VOL. 48, N. 3, pp. 183-188

Stafilov, T., Balabanova, B., Šajn, R. Bačeva, K., Boev, B. 2010. Geochemical atlas of Radoviš and the environs and the distribution of heavy metals in the air, Faculty of Natural Sciences and Mathematics, Skopje.

Walton, C., Philips, D., Serafimovski, T., Siderovski, K., Georgieva, M. and Ivanov, F., 2003a. Environmental Audit Report, Toranica Mine. Adam Smith Institute and Ministry of Environment and Physical Planing of the Republic of Macedonia. 40 p.

Walton, C., Philips, D., Serafimovski, T., Siderovski, K., Georgieva, M. and Ivanov, F., 2003b. Environmental Audit Report, Zletovo Mine. Adam Smith Institute and Ministry of Environment and Physical Planing of the Republic of Macedonia. 41 p.

Walton, C., Philips, D., Serafimovski, T., Siderovski, K., Georgieva, M. and Ivanov, F., 2003c. Environmental Audit Report, Sasa Mine. Adam Smith Institute and Ministry of Environment and Physical Planing of the Republic of Macedonia. 40 p.

TUFA VS. LACUSTRINE CARBONATES: SUITABLE PALAEOENVIRONMENTAL PROXIES?

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Abstract

Tufa barriers and lacustrine sediments from lakes formed behind the barriers in the upper part of the Krka River flow (Croatia) were studied as potential palaeoclimate archives. Stable isotope compositions of C and O ($\delta^{13}C$ and $\delta^{18}O$, respectively) of carbonate, as well as $\delta^{13}C$ of sedimentary organic carbon and dissolved inorganic carbon (DIC), and $\delta^{18}O$ of river and pore water were investigated. It was found that in two neighbouring lakes, the isotope thermometer would give misleading results since both carbonates as well as sedimentary organic matter represent two significantly different populations of samples, although the temperature and macro-environmental conditions are practically the same. Lacustrine carbonates are often used as palaeoclimate archives, however, several limitations should be considered: (1) high sedimentation rate (exceeding 1 cm/year) masks the primary temperature-dependent isotopic signal; (2) early diagenesis of sedimentary organic matter governs the carbonate equilibrium in the pore water, but the exchange between solid and dissolved carbonate pool can hardly be quantified; (3) in tufa precipitating rivers, it is not possible to distinguish between detritic and authigenic lacustrine carbonate precipitation, since both were formed from DIC of biogenic origin. Lacustrine sediments thus provide information on microenvironmental rather than regional environmental conditions.

Introduction

Tufas and authigenic sediments accumulated in lakes behind tufa barriers are often considered as potential environmental indicators, since the climatic conditions during the period of their growth, as well as discharge, precipitation, nutrient balance and anthropogenic influences are reflected in their morphological, geochemical and isotopic characteristics (Andrews and Brasier, 2005, and references therein). The stable oxygen isotope composition of tufa ($\delta^{18}O$), the distribution of trace elements such as Mg, Sr and Ba, and changes in the concentration and molecular composition of organic substances shall reflect the relative temperature changes that occurred during their formation (Pazdur et al., 1988; Coletta et al., 2001; Ihlenfeld et al., 2003). However, it was shown that the uncertainties of both isotopic and geochemical thermometers can be large, even exceeding 10°C, in particular when they are formed in rivers impacted by anthropogenic influences (Lojen et al., 2009). One serious drawback of palaeoclimatic studies based upon the chemical and isotopic composition of tufas is that precipitation is assumed to occur under equilibrium conditions, while in practice, this can seldom be confirmed; further, little or no information is available on the chemical and isotopic composition of the parent water during carbonate precipitation. In the present paper we compare barrage tufa and lacustrine carbonates formed in Krka River, Croatia, to elucidate whether any of them could potentially be suitable archive for palaeoenvironmental reconstruction of that area.

Environmental setting

Krka is a groundwater-fed karstic river, which receives considerable amounts of water through subsurface diffuse recharge, in particular in the middle part of the river course (Bonacci and Ljubenkov, 2005; Bonacci et al., 2006). A previous study (Lojen et al, 2004) reveals that except during extreme high water events the river water is supersaturated with respect to calcite and is degassing CO_2 along its entire 50 km course, and the massive tufa that is found in the river bed is formed under non-equilibrium conditions. The tufa deposition is a constant and dynamic process, depending upon many physicochemical factors, so the sedimentary processes of alternating barrage and lacustrine tufa formation reflect the fluvio-lacustrine dynamics of the river system. At the present time, Krka River is divided by 9 main and numerous small tufa barriers which caused formation of many lakes. The studied area is located in the upper part of the river, about 20 km downstream the spring, encompassing the approx. 2 km long section of Brljan lakes with 2 main basins. The maximum depth of the two larger lakes (Upper and Lower) is 15 and 8 m, respectively. The sedimentation rate in the Upper Lake, determined using ^{137}Cs method, is approx. 12 mm/year (Cukrov et al., in preparation).

Sampling and analyses

Hand samples of barrage tufa were collected at the closest cascades upstream and downstream the lacustrine section (Bilušića buk and Miljacka), and at accessible sites at the river bed in flow sections separating the lakes. Lacustrine sediment was collected manually by SCUBA diving using plastic corers.

Tufa samples were oven dried (50°C) and pulverized prior to analyses.

Sediment cores were cut into 2 - 4 cm sections in a nitrogen-filled glove bag to protect the samples from contact with air. All manipulations were performed either in the glove bag or in tightly closed containers. Interstitial water was extracted by centrifugation (4000 rpm), filtered through 0.45 μm membrane filters and kept refrigerated (4°C) in gas-tight glass vials with septa until further analyses. Samples for elemental analysis (Ca, Mg) were acidified with suprapure HNO_3. Remaining sediment was oven dried and processed in the same way as tufa.

Sediment samples were analysed for concentrations and stable isotope compositions of sedimentary organic carbon and nitrogen, as well as stable isotope compositions of C and O in carbonate. Pulverized samples were reacted in He-flushed vials with 100% H_3PO_4 at 25°C for 24 hours and CO_2 evolved was analysed using Europa 20-20 isotope ratio mass spectrometer with ANCA TG gas separation module. Isotope composition of sedimentary organic C ($\delta^{13}C_{org}$) was determined in samples digested in 1 M HCl, while $\delta^{15}N$ was determined in untreated sediment samples.

Interstitial water was analysed for total alkalinity using Gran titration method. Main cations (Ca^{2+} and Mg^{2+}) were determined using atomic absorption spectrometry. Concentration of dissolved inorganic carbon was calculated from pH and alkalinity using PhreeqM geochemical modelling programme.

Stable isotope composition of dissolved inorganic carbon and oxygen in water were determined using IsoPrime continuous-flow isotope ratio mass spectrometer with MultiFlow Bio equilibration unit. All isotope compositions are reported in relative δ values as deviations of heavy-to-light isotope ratios of samples from those of standards, expressed in permil (‰). Sedimentary carbon and oxygen isotope compositions are expressed vs. V-PDB, oxygen in water vs. V-SMOW standard and sedimentary N vs. air.

Results and discussion

Tufa

Downstream changes of $\delta^{13}C$ and $\delta^{18}O$ values of tufa are shown in Figure 1, where sites 8 and 0 represent the closest up- and downstream large barriers (Bilušića buk and Miljacka).

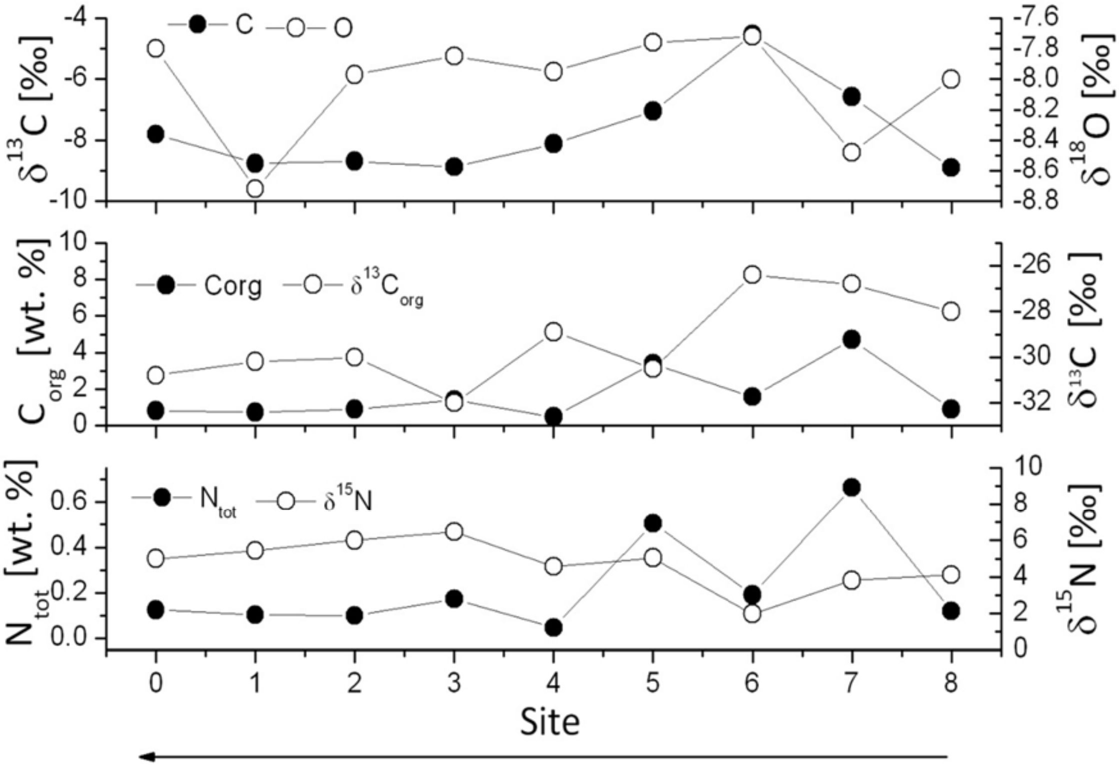

Fig. 1. Downstream variations in stable isotope composition of C and O in carbonate, sedimentary organic C and total sedimentary N in tufa; barriers 0 and 8 represent tufa from the closest up- and downstream big cascades; arrow denotes the river flow direction

It is evident that significant differences of some ‰ exist in both $\delta^{13}C$ and $\delta^{18}O$ values of barrage and river bed tufa. Samples 7 – 5 were taken in the Upper Lake (at the river inflow, at shore about 1 m above the lake level and at the outflow) and exhibited the highest $\delta^{13}C$ and $\delta^{18}O$ values of all analyses tufas; samples 4 and 3 were collected at the inflow and at the outflow into the Lower Lake, while samples 2 and 1 were collected in the river above and below the waterfall next to the Lower Lake. The higher values in the river bed tufa samples (reaching up to -5‰ for $\delta^{13}C$ and -7.7 ‰ for $\delta^{18}O$) are attributed to the presence of variable amount of detritic carbonate bedrock, consisting of marine limestone.

The concentration of C_{org} and N gradually decrease downstream. The $\delta^{13}C$ values of organic component decrease, following the general trend of SOM in the river (Lojen et al., 2004), while the $\delta^{15}N$ values increase, indicating the downstream increasing fraction of organic material of bacterial origin.

Pore water – sediment system

Downstream changes of main hydrochemical and isotopic parameters in Krka River were previously elaborated (Lojen et al., 2004, Lojen et al., 2009, Cukrov et al., 2011, in press). The $\delta^{18}O$ of river and lake water in the investigated area varied between -8.73 and -7.42 ‰ V-SMOW, while the pore water at all four investigated sites had a surprisingly uniform $\delta^{18}O$ value throughout the sediment column, -8.49 – -8.56 ‰ VSMOW, which is within the analytical error of the measurement. The pore water in all analysed samples was supersaturated with respect to calcite throughout the sediment column ($0.55 < SI_{ca} < 1.2$). A considerable difference was found between the sediments from the two lakes. Although the DIC concentrations at the lake bottom were very similar in both lakes, between 3.5 and 4 mM, the DIC depth profiles differed (Figure 2).

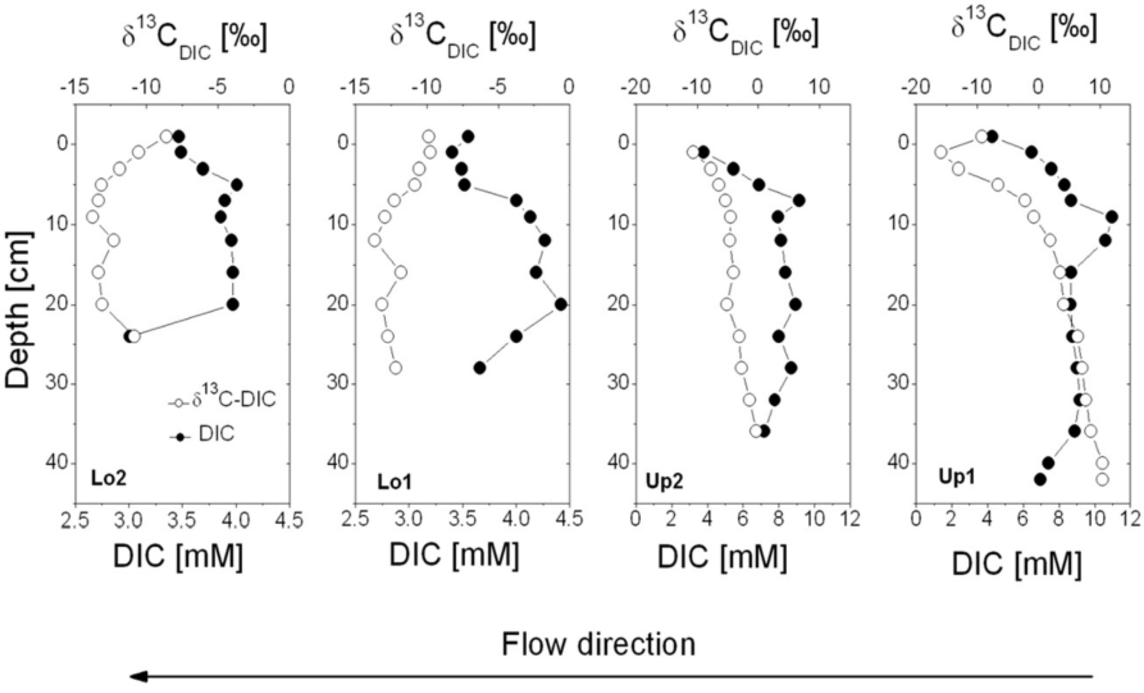

Fig. 2. Concentration of dissolved inorganic carbon (DIC) and its stable isotope composition ($\delta^{13}C_{DIC}$) in the sediment columns of Upper (Up1, Up2) and Lower Brljan Lake (Lo1, Lo2)

In the Upper Lake sediments, DIC concentration started to increase at or immediately below the sediment-water interface, reaching values of up to 10.3 mM in the depth segment of 8 – 10 cm (Up1, Fig. 2); initial increase in DIC concentration was accompanied by a considerable shift toward more negative $\delta^{13}C$-DIC values, indicating intensive oxic decomposition of sedimentary organic C. Below 2 cm, $\delta^{13}C$-DIC values started to increase, which is typical for methanogenic environments (LaZerte, 1981). The drop in DIC concentration below 10 cm is attributed to the onset of intensive calcite precipitation, which is also reflected in the decreasing $\delta^{13}C$ value of carbonate (Figure 3). At the sampling site located about 200 m downstream the Upper Lake (Up2), the shape of the DIC vs. depth profile is very similar, although the maximum DIC concentration and $\delta^{13}C$-DIC values are lower (Figure 2, Up2). With increasing depth, DIC production and carbonate precipitation seem to be more or less balanced. Completely different situation was observed in Lower Lake (Lo1 and Lo2). At site Lo1, close to the river inflow, DIC concentration remains constant in the upper 5 cm of the sediment column, indicating rather slow decomposition of sedimentary organic matter (calcite dissolution is not expected because of super saturation of pore water with respect to calcite). After the increase in the depth segment between 5 and 20 cm, the following decrease in DIC concentration is again accompanied by decreasing $\delta^{13}Cc_{arb}$ values as an indication of precipitation of authigenic ^{13}C-depleted carbonate(Figure 3).

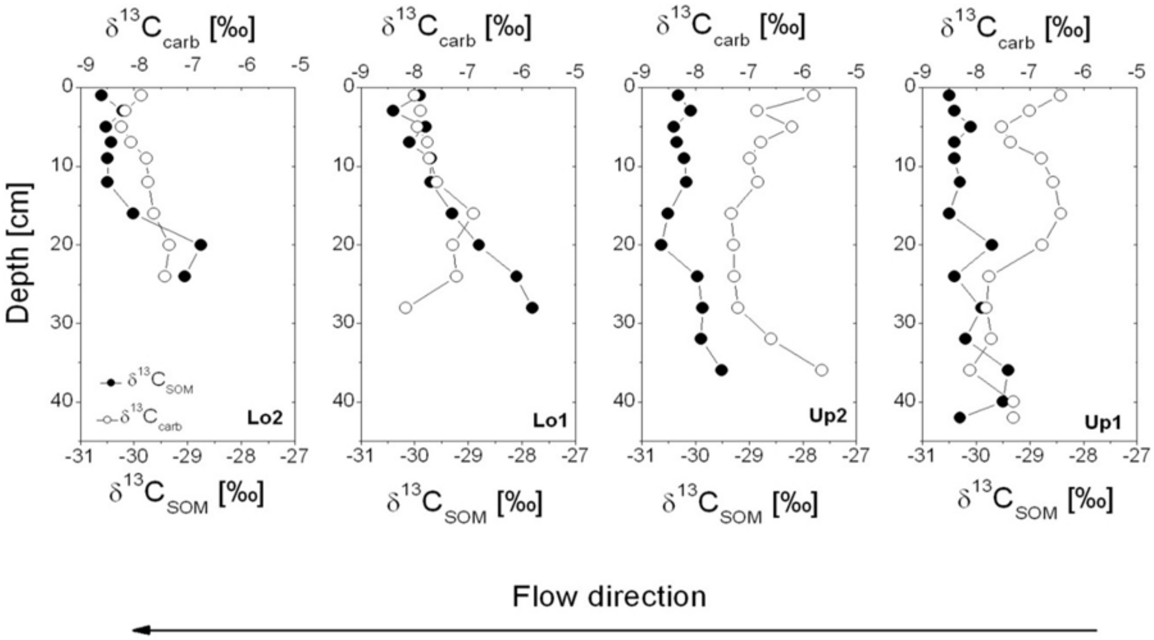

Fig. 3. Stable isotope compositions of carbon in carbonate and sedimentary organic matter in the sediment columns of Upper (Up1, Up2) and Lower Brljan Lake (Lo1, Lo2)

At the most downstream site, close to the outflow from the Lower Lake, increasing DIC concentration with depth is attributed to the decomposition of sedimentary organic matter and related decrease in δ^{13}C-DIC in upper 10 cm of the sediment column. As evident from Figure 3, the $\delta^{13}C_{carb}$ vs. depth profiles vary in a very similar way as δ^{13}C vs. depth profiles of sedimentary organic matter and are rather independent of the δ^{13}C-DIC variation (Figure 4).

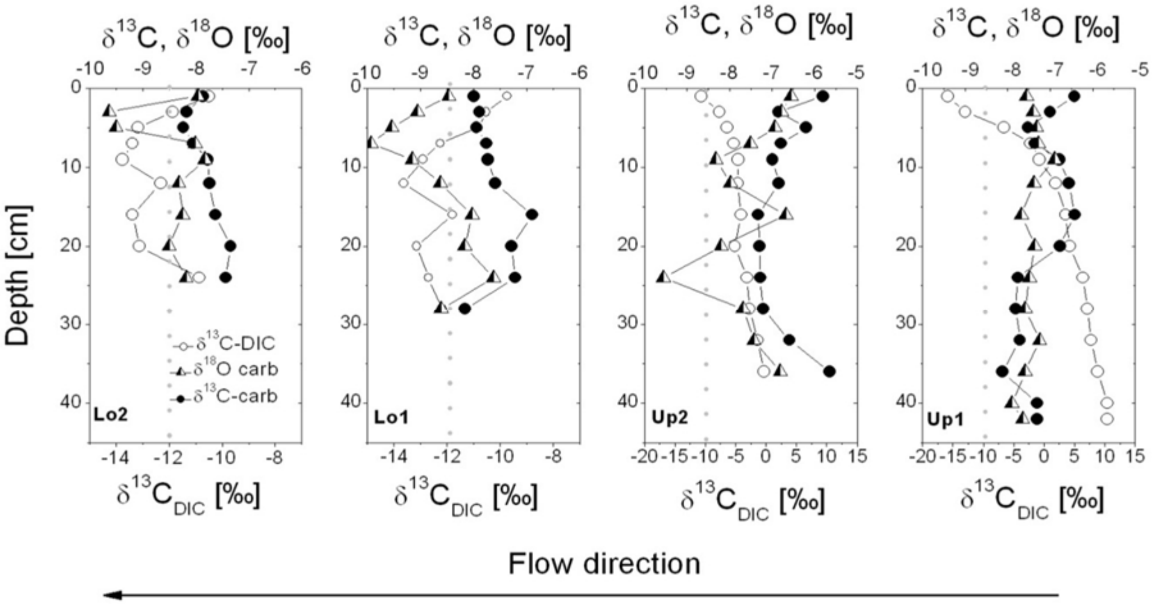

Fig. 4. Stable isotope composition of oxygen and carbon in carbonate and dissolved inorganic carbon in the sediment columns of Upper (Up1, Up2) and Lower Brljan Lake (Lo1, Lo2); grey line represents the δ^{18}O of pore water.

This indicates that the locus of carbonate precipitation is, as typical for tufa precipitating environments, at surfaces of organic detritic particles or extracellular mucopolysacharide polymers (Habdija et al., 2010), so that the ^{13}C-depleted DIC precipitates as $CaCO_3$ in microenvironments which are not affected by the bulk interstitial solution chemistry and isotopic composition of dissolved components.

The relation between $\delta^{18}O$ values of water and carbonate should in principle be temperature dependent; this would imply that-considering the stable $\delta^{18}O$ value if interstitial water-that the $\delta^{18}O$ values of authigenic carbonate should be stable, too. This is, however, not the case in any of the investigated sediments (Figure 4). On one hand, the fraction of authigenic carbonate is very difficult to determine because it has the same or very similar isotopic composition as tufa, which represents most of the detritic mineral fraction because of erosion of tufa barriers upstream the lake. On the other hand, the $\delta^{18}O$ is dependent not only upon the temperature, but also upon the precipitation rate (Dietzel et al., 2009), which can critically obscure the temperature record derived from $\delta^{18}O$ values of carbonate sediments precipitated in non-equilibrium conditions, which evidently govern the calcite precipitation in the sediment of Brljan Lakes.

References

Andrews, J.E., Brasier, A.T., 2005. Seasonal records of climatic change in annually laminated tufas: short review and future prospects. Journal of Quaternary Science 20 (5), 411-421.

Bonacci, O., Ljubenkov, I., 2005. New insights into the Krka river hydrology. Hrvatske vode 13 (52), 265-281 (in Croatian, with English abstract).

Bonacci, O., Jukić, D., Ljubenkov, I., 2006. Definition of catchment area in karst: Cases of the rivers Krčić and Krka, Croatia. Hydrological Sciences Journal 51 (4), 682-699.

Coletta, P., Pentecost, A., Spiro, B., 2001. Stable isotopes in charophyte incrustations: relationships with climate and water chemistry. Palaeogeography, Palaeoclimatology, Palaeoecology 173 (1-2), 9-19.

Cukrov, N., Tepić, N., Omanović, D., Lojen, S., Bura-Nakić, E., Vojvodić, V., Pižeta, I., 2011. Qualitative interpretation of physicochemical and isotopic parameters in the Krka River (Croatia) assessed by multivariate statistical analysis. International Journal of Environmental Analytical Chemistry, in press, DOI/10.1080/03067319.2010.550003.

Dietzel, M., Tang, J., Leis, A., Köhler, J.S., 2009. Oxygen isotopic fractionation during inorganic calcite precipitation – Effects of temperature, precipitation and pH, Chemical Geology 268, 107-115.

Habdija, I., Stilinovć, B., Primc Habdija, B., Matoničkin Kepčija, R., Špoljar, M., Miliša, M., Sertić Perić, M., 2009. A review of research on faunistic and ecological diversity of protozoans and invertebrates in aquatic habitats of tufa barriers and lakes in the National park Plitvice Lakes . In: Zbornik radova, Znanstveno-istraživački skup Nacionalnog parka Plitvička jezera, 15.-16.11.2009, Javna ustanova "Nacionalni park Plitvička jezera", ISBN 978-953-96146-4-3.

Ihlenfeld, C., Norman, M.D., Gagan, M.K., Drysdale, R.N., Maas, R., Webb, J., 2003. Climatic significance of seasonal trace element and stable isotope variations in a modern freshwater tufa. Geochimica et Cosmochimica Acta 67 (13), 2341-2357.

LaZerte, B., 1981. The relationship between dissolved carbon dioxide and its stable isotope ratio in aquatic sediments. Geochim. Cosmochim. Acta 45, 647–656.

Lojen, S., Dolenec, T., Vokal, B., Cukrov, N., Mihelčić, G., Papesch, W., 2004. C and O stable isotope variability in recent freshwater carbonates (River Krka, Croatia). Sedimentology 51 (2), 361-375.

Lojen, S., Trkov, A., Ščančar, J., Vázquez-Navarro, J.A., Cukrov, N., 2009. Continuous 60-year stable isotopic and alkali element records in a modern laminated tufa (Jaruga hydroelectric power plant, river Krka, Croatia). Chemical Geology, 258, 242-250.

Pazdur, A., Pazdur, M.F., Starkel, L., Szulc, J., 1988. Stable isotopes of Holocene calcareous tufa in southern Poland as palaeoclimatic indicators. Quaternary Research, 30 (2), 177-189.

HEAVY METALS DISTRIBUTION IN SOIL FROM KIČEVO BASIN, REPUBLIC OF MACEDONIA

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Abstract

Data from the study of spatial distribution of various elements in surface soil over of the Kičevi basin, Republic of Macedonia, known for its coal mine and thermoelectical power plant activities are reported. The investigated region is covered by a sampling grid of 2×2 km^2; with the denser grid in the urban zone and around the thermoelectric power plant (1×1 km^2). In total 52 top soil samples (0–5 cm) were collected. The samples were analysed by inductively coupled plasma - atomic emission spectrometry (ICP-AES) Data analysis and construction of maps were performed using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. Three natural geochemical associations has been defined (Cr-Ni-Li-Co-Fe-As; Al-Ca-Mg-Sr and Ba-K-Cu).

Introduction

The abundance of heavy metals in soil has been increased dramatically by the accelerated rate of extraction of minerals and fossil fuels and by highly technological industrial processes. Rapid increases of trace metal concentrations in the environment are commonly coupled to the development of exploitative technologies. Urban and regional contamination of soil occurs mainly in mining and industrial regions and within centres of large settlements (Kabata-Pendias and Pendias, 2001). Because of heterogeneity and ceaseless changing of urban areas, it is necessary first to understand the natural distribution. However, there are cases when the industrial enterprises, especially mining and metallurgical plants, situated near cities can increase the pollution. It is obvious from the papers published recently that mining and metallurgical activities lead to enormous soil contamination (Kabata-Pendias and Pendias, 2001), which is the case with some regions in the Republic of Macedonia (Barandovski et al., 2008; Stafilov et al., 2010a, 2010b; Balabanova et al., 2011).

The aim of this study is to present the results of a first systematic investigation of spatial distribution of different chemical elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn) in surface soil over of the Kičevo region known for its coal mine and thermoelectrical power plant "Oslomej" and to assess the size of the area eventually affected by the thermoelectrical power plant situated near the town.

Geographic description

Kičevo is settled in the valley of Kičevo in the south-eastern foothills of Bistra Mountain (Fig. 1) in the western part of Macedonia. Kičevo is surrounded by mountains and forests, and is a town that is attractive not only of its natural beauties, but also its anthropogeneous and cultural values. According to the 2002 census, Kičevo had a population of 30,138 inhabitants.

The whole region with the community of Kičevo, Oslomej and Zajas has about 52,000 people and contains an extraordinary diversity of social and economic patterns. Kičevo is an important industrial center in this part of Macedonia, due to the iron mine in Tajmište (closed at the moment), the coal mine and the thermoelectric power plant Oslomej. Kičevo is a mining town that started to develop very intensively after the 2nd World War. Main feature of the economy in the region is the mining and thermoelectric power plant REK "Oslomej". It is the first facility of its kind built in the country. REK "Oslomej" has the installation capacity is 125 MW with net annual production of around 700 GWh. REK Oslomej began its production in 1980 and has had excellent production results. It provides for about 9% of the total electrical energy production in the Republic of Macedonia.

The study area is located in the western part of the Republic of Macedonia with surface of *ca.* 12 km (W–E) × 16 km (S–N), in total of 148 km^2, limited with coordinates N: 41°29'57"–41°38'43" and E: 20°54'35"–21°03'22" (Figs. 1 and 2). The altitude varies between 570 and 1260 m. The area of the different land uses is: cultivable area covers 64 km^2 (43 %), non-cultivable area (mainly forests) 68 km^2 (46 %), settlements 9.9 km^2 (6.7 %) and area of Oslomej open pit and thermoelectric power plant 6.1 km^2 (4.3 %).

Geological description

The geological description (Fig. 3) was written according to Petkovski and Ivanovski (1973), and Dumurdjanov et al. (1972). The study area is a part of western Macedonian zone, which belongs to the Inner Dinnarids characterized by strong structural forms such as thrusts, syncline, anticline, etc. The structure has a direction NW-SE. Two types of orogeny strongly influenced a development of the zone. The Hercynian (Variscan) Orogeny has influence on Palaeozoic rocks which are regionally metamorphosed and fluted but on other side the Alpine Orogeny caused very strong metamorphism, intensive fluting and conversion of older structures. Subsequent radial tectonic has resulted in formation of anticline structures and basins (The Kičevo basin), that were filled by younger Pliocene and Quaternary sediments.

The oldest rocks belong to the Lower Palaeozoic (Pz) metamorphic complex, mostly consist phyllitoid with inclusion of metasandstone quartzite and carbonatic schist. The Lower Palaeozoic rocks are developed in the north of the study area. Devonian (D) rocks lies over this complex. These are phyllitoides, sandstone and conglomerate, quartzite and marble. The Devonian rocks outcrop in the southern part of the study area. Over the Palaeozoic beds are developed the Mesozoic rocks. There are represented by the Jurassic diabase rocks (penetrations or inclusions of magmatic rocks), which outcrop on very limited part on the south. Middle and Upper Pliocene sediments are developed in the central part of the study area (the Kičevo basin) and consist of marl, sand and clay with coal layers. Pliocene sediments were developed in the central part of the study area. Alluvial sediments cover the flood plains along the rivers Treska, Zajaska and Temnica that contain mainly coarse grain material gravel, sand and sandy clay.

From 148 km^2 of the studied area, the Quaternary deposits are found on 41.4 km^2 (28 % of study area), Pliocene marl, clay, sand and gravel on 28.9 km^2 (20 %), Jurassic diabase on 1.1 km^2 (<1 %), Devonian marble on 8.3 km^2 (5.6 %), Devonian quartzite on 1.3 km^2 (<1 %), Devonian phyllitoides on 15.7 km^2 (11 %), Devonian sandstone and conglomerate on 16.4 km^2 (11 %) and Lower Palaeozoic shists on 34.9 km^2 (23%).

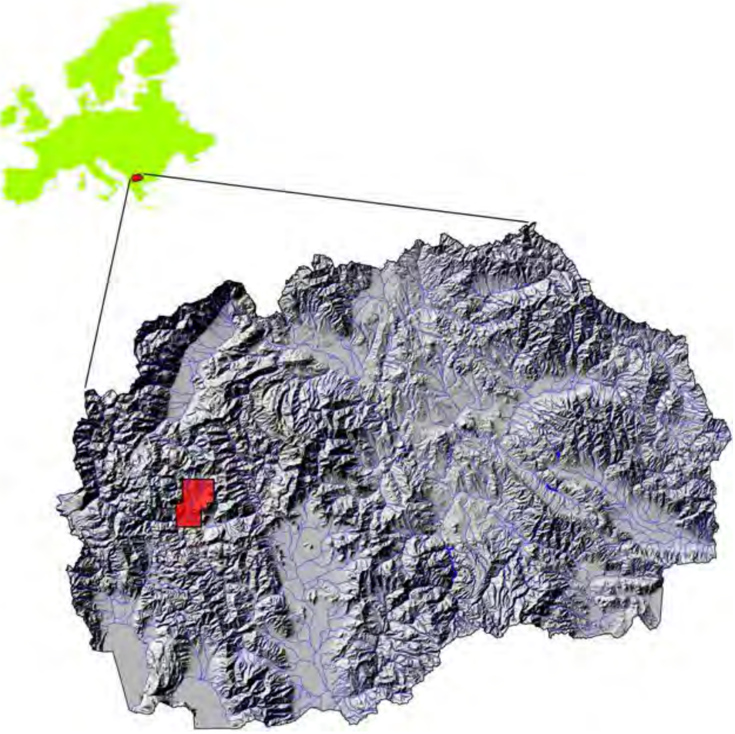

Fig. 1. Location of the study area

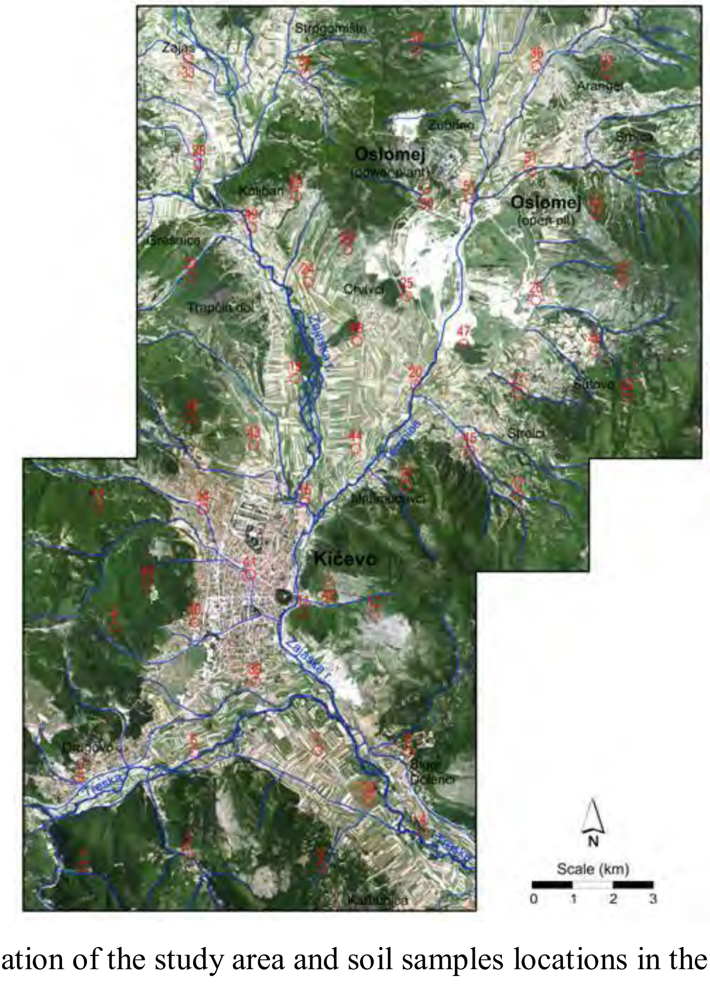

Fig. 2. Location of the study area and soil samples locations in the Kičevo area

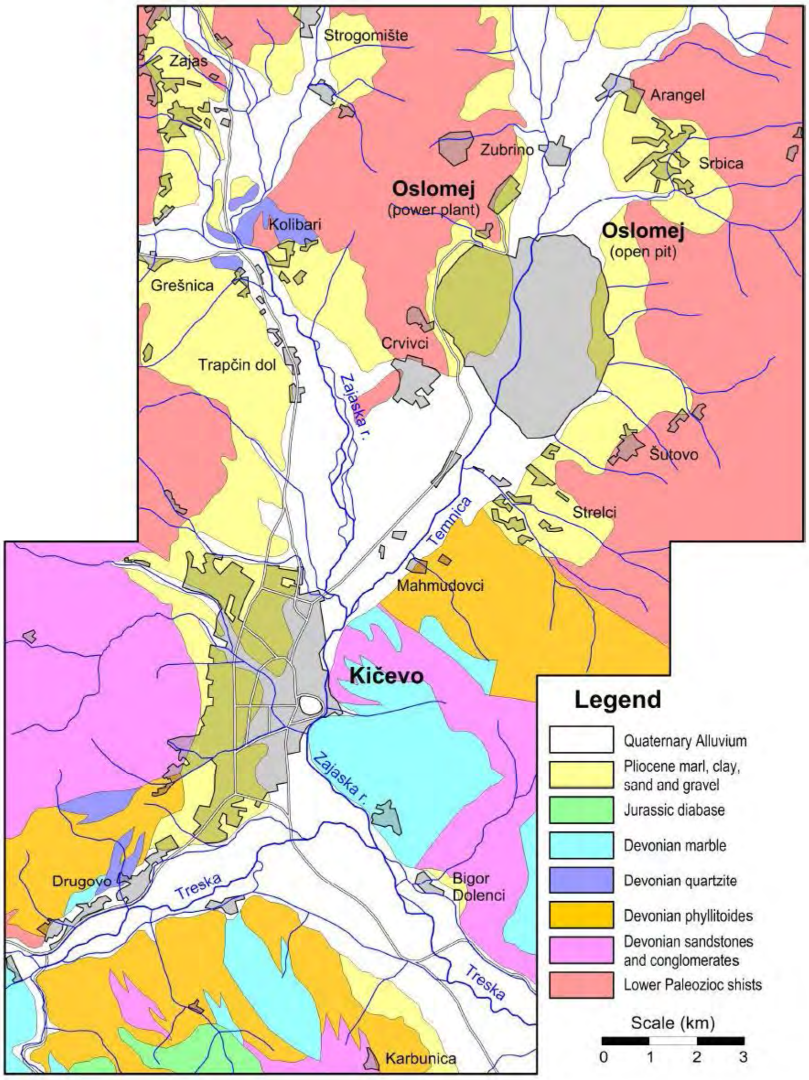

Fig. 3. Lithological map of the Kičevo area

Material and methods

Sampling

Samples of surface soils (0-5 cm) were collected according to the European guidelines for soil pollution studies (Salminen et al., 2005), and also according to our experience (Šajn, 2005, 2006; Stafilov et al., 2010a, 2010b). The study area (148 km^2) is covered by a sampling grid of 2×2 km^2 but in the urban zone of Kičevo and around the Oslomej thermoelectric power plant the sampling grid is denser, 1×1 km^2 (Fig. 2). Altogether 52 soil samples were collected. In each sampling point soil samples were collected as topsoil (0–5 cm). The possible organic horizon was excluded. One sample represents the composite material collected at the central sample point itself and at least four points within the radius of 10 m around it towards N, E, S and W. According to the basic lithological units, 10 sampling sites are located on the area of Quaternary alluvium of the Treska River, 14 on the Quaternary alluvium of the Zajaska and Temnica rivers, 10 on Pliocene marl, clay, sand and gravel, 3 on Devonian sandstone and conglomerate, 4 on Devonian marble, 6 on Devonian phyllitoides and 10 on Lower Palaeozoic shists.

Sample preparation and analysis

The soil samples were air dried indoors at room temperature for about two weeks. Then they were gently crushed, cleaned from extraneous material and sifted through a plastic sieve with 2 mm mesh (Davis, 1986). The shifted mass was quartered and milled in agate mill to an analytical grain size below 0.125 mm. For digestion of soil samples, open wet digestion with mixture of 4 acids (HNO_3, HF, $HClO_4$ and HCl) was applied (Balabanova et al., 2011). The obtained solutions of soil samples were analyzed with the application of atomic emision spectrometer with inductively coopled plasma Varian 715ES.

Results and discussion

Data processing and drawing of maps

Data analysis and production of maps were performed on a PC using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. All field observations, analytical data and measurements were introduced to the data matrix. For each observation there are 45 variables: sample identification number, sampling material type, geographic coordinates (X, Y, Z), kind of analysis, land use, basic lithological units, level of soil pollution and determination of 19 analyzed elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn) with ICP-AES method ($n = 52$). The methods of parametric and nonparametric statistics were used for the data analysis (Davis, (1986). The basic statistics data for the 19 selected chemical elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn) and the average of elements are shown in Table 1.

Table 1. Descriptive statistics of measurements (n = 52) Values of Al, Ca, Fe, K, Mg and Na are in %, remaining elements in mg/kg.

	Dis.	X	X_g	Md	min	max	s	CV	s_x
Al	Log	1.7	1.5	1.4	0.53	4.7	0.92	54	0.13
Ca	Log	0.54	0.30	0.24	0.042	3.1	0.66	122	0.091
Fe	Log	2.9	2.8	2.8	1.5	5.4	0.66	23	0.092
K	N	1.4	1.4	1.4	0.63	2.2	0.34	23	0.047
Mg	Log	0.64	0.57	0.59	0.20	1.6	0.31	49	0.043
Na	Log	0.55	0.44	0.50	0.064	1.6	0.36	65	0.050
As	N	9.3	6.3	7.8	0.13	34	7.2	77	1.0
Ba	Log	390	380	380	160	890	120	31	17
Cd	Log	0.47	0.42	0.42	0.17	0.99	0.21	44	0.029
Co	Log	15	11	11	0.59	60	11	78	1.6
Cr	Log	44	41	43	13	110	17	38	2.4
Cu	Log	17	15	14	5.4	53	8.6	51	1.2
Li	Log	14	12	11	2.5	33	7.6	56	1.1
Mn	Log	760	700	690	210	2600	370	48	51
Ni	Log	21	19	18	5.5	56	10	49	1.4
Pb	Log	96	64	71	1.7	430	80	84	11
Sr	Log	17	15	15	5.8	45	9.1	55	1.3
Zn	Log	150	110	97	11	1700	230	154	31

Dis. – distribution (N – normal, Log – lognormal); X – mean; X_g – geometrical mean; Md – median; min – minimum; max – maximum; s – standard deviation; CV – coefficient of variation (%); s_x – standard error of mean; A – skewness; E – kurtosis

The multivariate R-mode factor analysis (Davis, (1986) was used to reveal the associations of the chemical elements. Factor analysis (FA or PCA) derives from numerous variables a smaller number of new, synthetic variables called factors. The factors contain significant information about the original variables, and they may have certain meanings. The factor analysis was performed on variables standardized to zero mean and unit of standard deviation (Reimann et al., 2002). As a measure of similarity between variables, the product-moment correlation coefficient (*r*) was applied. For orthogonal rotation, the varimax method was used. In the factor analysis, 52 samples of the topsoil (0–5 cm) and analysis of 13 chemical elements were considered.

From the multivariate R-mode factor analysis, 5 chemical elements (Cd, Mn, Na, Pb and Zn) were eliminated from further analysis because they have low share of communality or low tendency to form independent factors. With the factor analysis the distribution is decreased to three synthetic variables (F1 to F3), have connected in regard to geochemical similarities, which are include 74.3 % of the variability of the treated elements (Table 2).

The universal kriging method with linear variogram interpolation (Davis, 1986) was applied for construction of the areal distribution maps of the 19 particular elements and the factor scores (F1–F3) in topsoil (0–5 cm). The basic grid cell size for interpolation was 20×20 m. For class limits the percentile values of distribution of the interpolated values were chosen. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100 (Fig. 4-6).

Table 2. Matrix of dominant rotated factor loadings (n = 52, 13 selected elements). Bold letters represent anthropogenically distributed geochemical association

Element	F1	F2	F3	Com
Cr	**0.88**	0.07	0.13	79.5
Ni	**0.83**	0.31	0.31	87.6
Li	**0.77**	0.22	0.33	75.0
Co	**0.73**	-0.06	-0.09	55.1
Fe	**0.68**	0.15	0.46	70.1
As	**0.66**	-0.10	0.22	49.5
Ca	0.00	**0.92**	0.04	84.1
Sr	0.11	**0.87**	0.16	78.6
Mg	0.11	**0.85**	0.21	78.3
Al	0.04	**0.83**	0.24	75.2
Ba	0.23	0.13	**0.84**	78.3
K	0.09	0.21	**0.84**	76.5
Cu	0.40	0.31	**0.73**	78.0
Var	28.8	25.8	19.7	74.3

F1 … F3 – Factor loadings; Com – Communality (%); Var – Variance (%)

Chemical elements in soils of the Kičevo area

The distributions of elements that reflect natural processes are indicated by elements that are rarely or never included industrial processes. Their contents usually change gradually across the landscape and depend on the geological background. Following the results of factor analysis (Table 2) and the trends shown on the geochemical maps (Figs. 4-6), three natural geochemical associations in soil has been defined.

Geochemical association Cr-Ni-Li-Co-Fe-As

The most characteristic association links As, Co, Cr, Fe, Li and Ni, which are assembled in the Factor 1 (Table 2, Fig. 4). The strongest Factor 1 contains high values of previously mentioned elements, explaining 29 % of the total variability within the data (the 13 selected chemical elements). Their sources are mainly natural phenomena, such as rock weathering and chemical processes in soil. In addition, the distribution of Factor 1 scores (As, Co, Cr, Fe, Li and Ni) in the topsoil is closely dependent on the lithology. Their highest contents were found in areas of the Devonian sandstone and Quaternary deposits of the Treska River and their lowest values in area of the Lower Palaeozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers. Those chemical elements are connected mostly to the sandy fraction in soil.

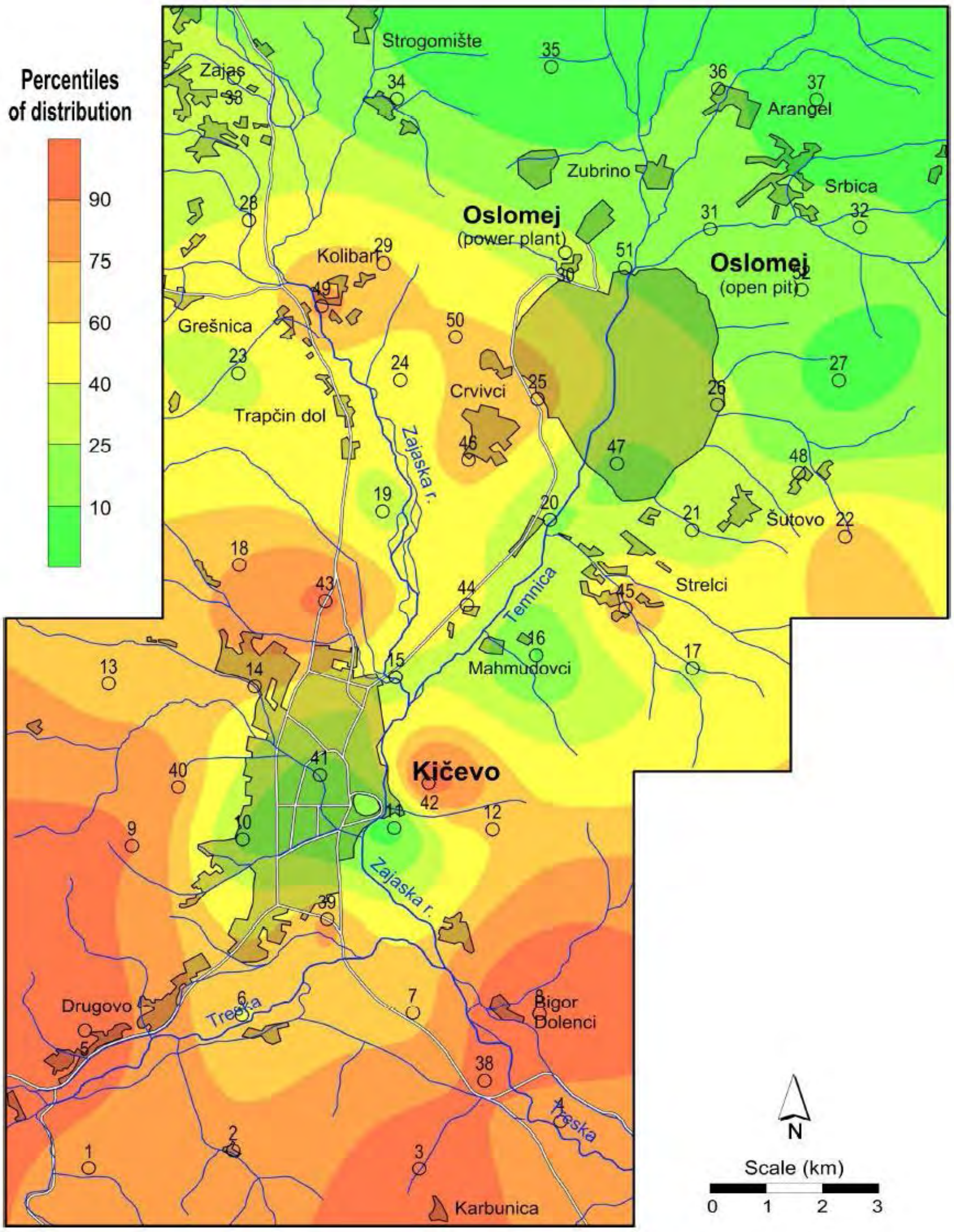

Fig. 4. Spatial distribution of factor 1 scores (Cr, Ni, Li, Co, Fe and As) in topsoil

Geochemical association Ca-Sr-Mg-Al

The association illustrated by Factor 2 associates Al, Ca, Mg and Sr. The second strongest Factor 2 contains high values of aforementioned elements, explaining 26 % of the total variability (Table 2). Areal distribution of the Factor 2 scores in topsoil is provided in Fig. 5. Similarly to the distribution of the Factor 1 scores, the spatial distribution of Factor 2 scores (Al, Ca, Mg and Sr) in topsoil closely depends on the lithology. Their highest contents were found in areas of the Devonian marble and Quaternary deposits of the Treska River and their lowest values, same as in the Factor 1, in area of the Lower Palaeozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers (Fig. 5). The elements from this factor are connected to the carbonitic minerals in soil, representing a product of marbles weathering processes.

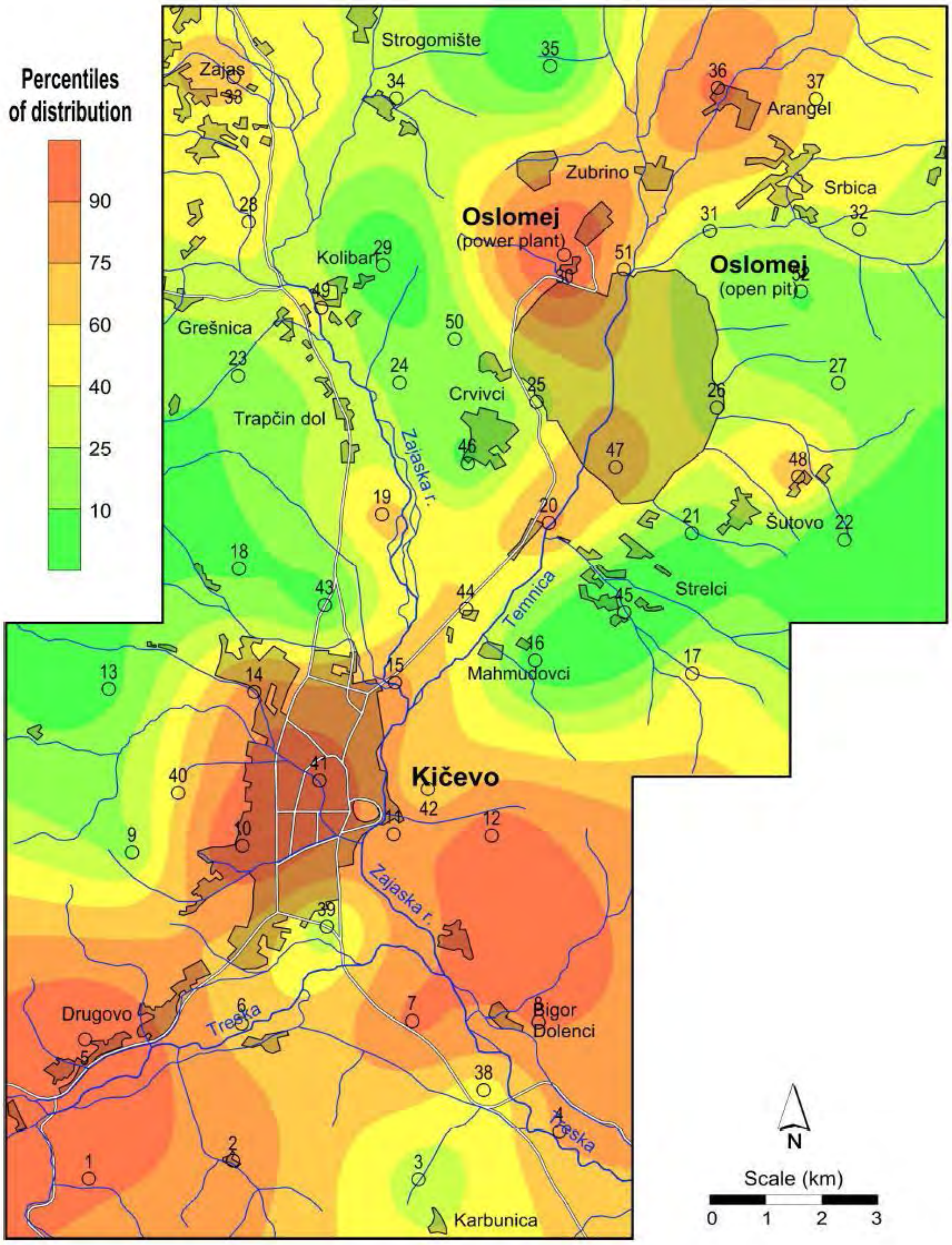

Fig. 5. Spatial distribution of factor 2 scores (Ca, Sr, Mg and Al) in topsoil

Geochemical association Ba-K-Cu

The third naturally distributed geochemical association consists Ba, Cu and K, chemical elements that are also little affected by anthropogenic activities. The Factor 3 contains high values of the mentioned elements, explaining 20 % of the total variability within the data (Table 2). Areal distribution of the Factor 3 scores in topsoil is shown in Fig. 6. Distribution of the Factor 3 scores (Ba, Cu and K) in topsoil also depends on the lithology (Fig. 6). Their highest contents were found in areas of the Devonian phyllitoides and their lowest values in area of the Lower Paleozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers, same as in F1 and F2. Those elements are connected to the clayey fractions.

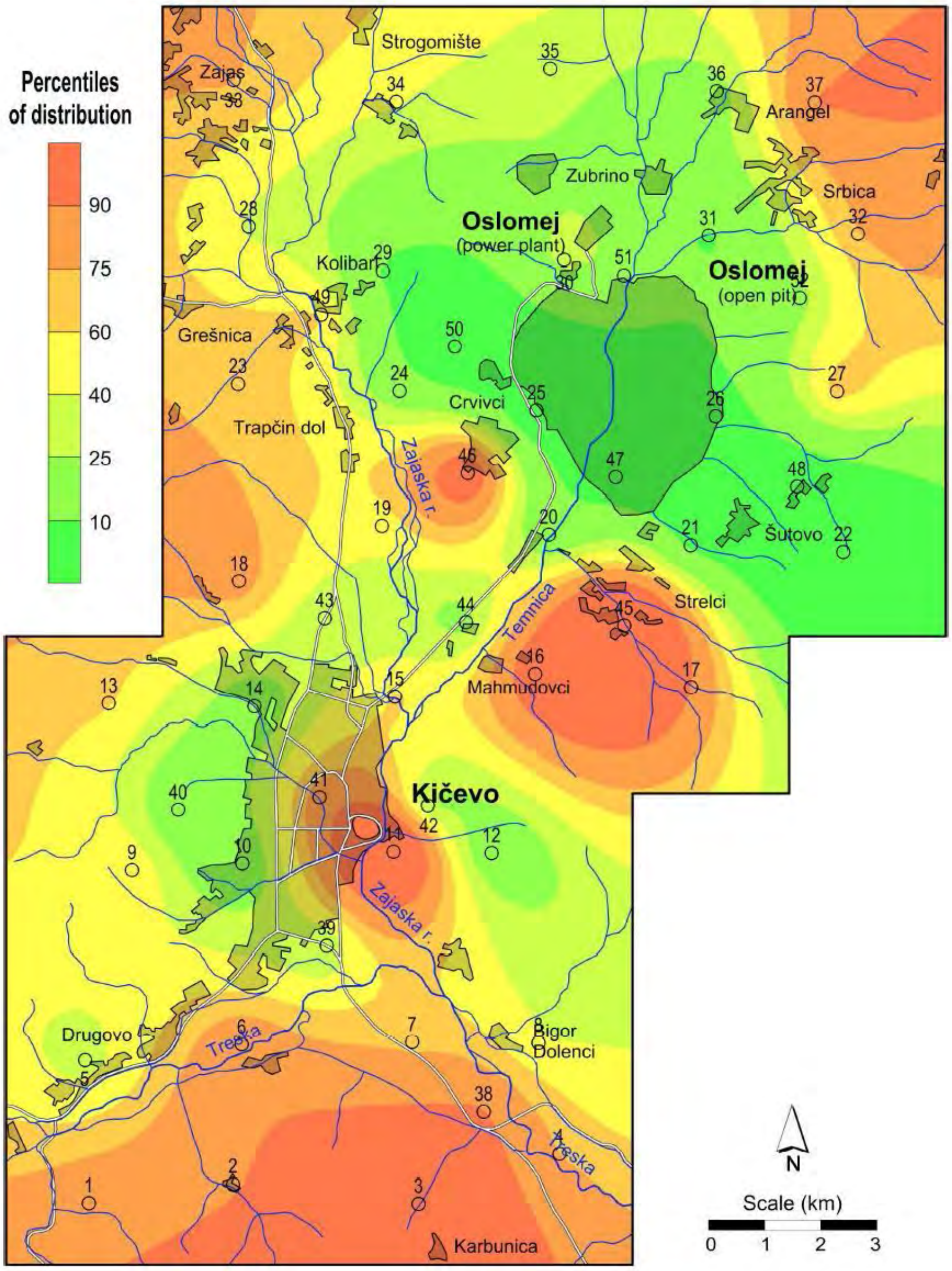

Fig. 6. Spatial distribution of factor 3 scores (Ba, K and Cu) in topsoil

Conclusion

Following the results of factor analysis and the trends shown on the geochemical maps, three natural geochemical associations in soil has been defined. The strongest Factor 1 contains high values of As, Co, Cr, Fe, Li and Ni. Their sources are mainly natural phenomena and closely dependent on the lithology. Their highest contents were found in areas of Devonian sandstone and Quaternary deposits of the river Treska and their lowest values in area of the Lower Palaeozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers. The association illustrated by Factor 2 (Al, Ca, Mg, Sr) has the highest and lowest values in the similar areas as it was found for the Factor 1. The elements from this factor are connected to the carbonitic minerals. The distribution of the Factor 3 (Ba, Cu, K) also depends on the lithology. Their highest values are in areas of the Devonian phyllitoides and the lowest in area of the Lower Paleozoic shists, Pliocene sediments and Quaternary deposits of the Zajaska and Temnica rivers. These elements are connected to the clayey fractions.

References

Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K. (2011). Distribution of chemical elements in attic dust as reflection of lithology and anthropogenic influence in the vicinity of copper mine and flotation, *Archives of Environmental Contamination Toxicology*, **61**, 173–184.

Barandovski, L., Cekova, M., Frontasyeva, M.V., Pavlov, S.S., Stafilov, T., Steinnes, E., Urumov, V. (2008). Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique, *Environmental Monitoring and Assessment*, **138**, 107–111.

Kabata-Pendias, A., Pendias, H. (2001). *Trace Elements in Soil and Plants*, Third Edition, CRC Press, Boca Raton.

Davis, J.C. (1986). *Statistic and Data Analysis in Geology*, Willey in Sons, New York.

Dumurdjanov, N., Stojanov, R., Petrovski, K. (1972). *Basic geological map of SFRJ, sheet Kruševo*, M 1:100,000 (map & interpreter), Federal Geological Survey, Beograd.

Petkovski, P., Ivanovski, T. (1973). *Basic geological map of SFRJ, sheet Kičevo*, M 1:100,000 (map & interpreter), Federal Geological Survey, Beograd.

Reimann, C., Filzmoser, P., Garrett, R.G. (2002). Factor analysis applied to regional geochemical data: problems and possibilities, *Applied Geochemistry*, **17**, 185–206.

Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. (2005). *Geochemical Atlas of Europe,* Part 1, *Background Information, Methodology and Maps*, Geological Survey of Finland, Espoo.

Šajn, R. (2005). Using attic dust and soil for the separation of anthropogenic and geogenic elemental distributions in an old metallurgic area (Celje, Slovenia), *Geochemistry: Exploration, Environment, Analysis*, **5**, 59–67.

Šajn, R. (2006). Factor analysis of soil and attic-dust to separate mining and metallurgy influence, Meza Valley, Slovenia, *Mathematical Geology*, **38**, 735–747.

Stafilov, T., Šajn, R., Pančevski, Z., Boev, B., Frontasyeva, M.V., Strelkova, L.P. (2010a). Heavy metal contamination of surface soils around a lead and zinc smelter in the Republic of Macedonia. *Journal of Hazardous Materials,* **175**, 896–914.

Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski, M., Lepitkova, S. (2010b). Distribution of some elements in surface soil over the Kavadarci Region, Republic of Macedonia, *Environmental Earth Sciences*, **61**, 1515–1530.

SPATIAL DISTRIBUTION OF ^{137}Cs IN THE SOILS OF THE REPUBLIC OF MACEDONIA

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ABSTRACT

Determination of the spatial distribution of the ^{137}Cs, resulting from atmospheric fallout (nuclear bomb testing, Chernobyl accident) in the surface soil of the Republic of Macedonia was a result of a systematic survey that was performed during 2007 – 2010. From the sites selected all over country area, 213 samples were collected from undisturbed soils at a depth of 0–20 cm. The measurements engaged gamma ray spectrometry. The values of ^{137}Cs specific activity were found to be in a narrow range between practically zeros all the way to 100-178 Bq kg^{-1} obtained for higher altitudes. The arithmetic and geometric mean values of ^{137}Cs specific activity were evaluated to be: 38 Bq kg^{-1} and 27 Bq kg^{-1}, respectively. Based on the conducted research, the spatial distribution of the ^{137}Cs in the surface soils was found to be different for the various regions of the country. Correlation was found to be significant with the elevation and longitude of the area.

1. INTRODUCTION

The main sources for the man-made radioactive materials, dispersed in the environment have been the nuclear weapons tests, performed in the 1960s as well as the reactor accident in Chernobyl in 1986 (1). As a results of later, the world has became widely contaminated with radionuclides of artificial origin. One of these long lived isotopes, ^{137}Cs, is still eminent in the environment predominately distributed in the surface soil, as a result of radioactive fallout from the atmosphere (2). As the ^{137}Cs approaches the earth's surface, it is rapidly and tightly adsorbed by fine particles of soil. After being adsorbed by soil, ^{137}Cs reveals a limited mobility by the chemical processes, and its redistribution in landscape is due to the soil movement due to physical processes (3). In addition to being the main source of continuous radiation exposure to human, soil acts as a medium of migration and therefore transferring the radionuclide to the biological systems. Hence, it is the basic indicator of radiological contamination in the environment (4)

The Chernobyl disaster had caused contamination in many countries. Regions affected by radioactive fallout included not only Ukraine itself but also many European countries. Following the accident, intensive large-scaled radiological investigations of the environmental samples were initiated worldwide, in order to define the global contamination level. As a result, an Atlas of caesium deposition on Europe after the Chernobyl accident in 1998 from the European Commission was published (5).

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This paper presents the data from the first systematic post-Chernobyl investigations of ^{137}Cs spatial distribution in the area of the Republic of Macedonia. Additionally, a correlation between specific activity of ^{137}C and elevation (altitude above the sea level), longitude and latitude were observed.

2. REGION OF INVESTIGATION

The Republic of Macedonia is located in the central part of the Balkan Peninsula, at the geographical coordinates between latitudes 40° and 43° North, and mostly between longitudes 20° and 23° East (a small area lies east of 23°). The country is 25 713 km^2 in area. More than 50% of the total area is mountain massive and only 2.5% confines urban or industrial land. From the topographic map (Figure 1), one could see spatially a variable topography and diversity in the elevation.

Figure 1. Topographic map of Republic of Macedonia
(downloaded from: http://maps.grida.no/go/graphic/the-former-yugoslav-republic-of-macedonia-fyrom-topographic-map - Source: The Times Atlas of the World)

Moving from south towards north, three climatic zones can be evident: moderate mediterranean, mountain and moderate continental climate. According to the statistics from the State Office for Statistics form 31.12.2008, the population of the Republic of Macedonia was 2 048 619 (6).

3. METHODOLOGY OF INVESTIGATION

3.1. Soil sampling and preparation

For data and results presentation, the regional division of the country in statistic regions is used. According to the division, since 2007, Republic of Macedonia has had 8 statistic regions: Polog (POL); Southwest (SW); Pelagonija (PEL); Skopje (SKO); Vardar (VAR); Southeast (SE); East (EAST); Northeast (NE).

A total of 213 surface soils, from sampling locations of the study area shown in figure 1, at 20cm depth (7) were collected during 2007 – 2010. A Global Positon System (GPS) was used to determined geographical coordinates. The samples were taken from uncultivated fields and sampling stations were chosen in/or close to populated areas. Therefore, the most of the sampling locations, where covered by some type of vegetation, such as grass or small bushes.

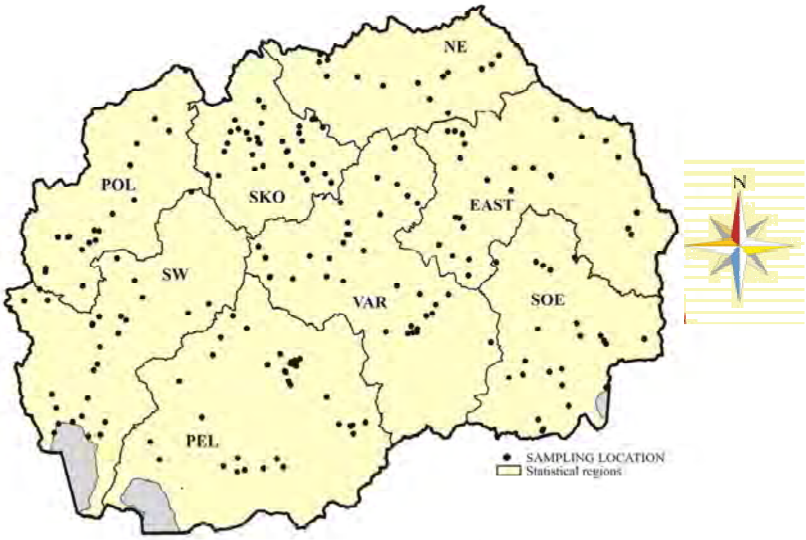

Figure 2. Sampling locations within the territory of the Republic of Macedonia. Statistical regions are divided with black lines.

All samples were grinded and then dried at 105°C temperature for the time until the moisture of the sample was completely removed. The dried samples were then hand grounded in a large ceramic mortar and passed through a sieve, before 500 ml volume was transferred to the Marinelli beaker and weighed before the gamma spectrometry measurements.

3.2. Gamma spectrometry measurements

The p-type HPGe gamma spectrometer with a 25 % relative efficiency and a resolution of 1.79 keV at 1.33 MeV linked up to a 8192 channels digital analyser, was used for gamma spectrometry measurements. The spectral analysis is performed by widely used gamma analysis software - GENIE 2000. The system was calibrated with mixed calibration standard sources MBSS2 from the Czech Metrological Institute. For the purposes of the quality assurance, verification of measured method was performed by using standard reference materials.

The specific activity of the ^{137}Cs, was determined from its 661.66 keV line. The total relative combined uncertainty of each measurement was less than 5%, at the 68% significance level (8).

4. RESULTS AND DISCUSSION

The gamma spectrometry allows both qualitative identification and quantitative determination of the radionuclide in the sample. All the data were compiled into Microsoft Excel spreadsheets and the statistical analysis were made with XLSTAT Pro 7.5.

Table 1 shows the descriptive statistics for ^{137}Cs specific activity in Bq kg^{-1}, for the 213 soil samples obtained due to gamma spectrometry measurements. The presentation includes the minimum, maximum, median, arithmetic mean, standard deviation of the mean value, geometric mean and standard deviation of the geometric mean.

Table 1: Statistics of specific activity of ^{137}Cs in soil samples

	A (Bq kg^{-1}) ^{137}Cs
Minimum value	0.23
Maximum value	178
Median value	29
Arithmetic mean	38
Standard deviation	31
Standard deviation of the mean value	2.13
Geometric mean	27
Standard deviation of the geometric mean	2.58

The frequency distribution of the results is presented on Figure 3 and it appears to be typical for the distribution of the man-made isotopes in the environment. Kolmogorov-Smirnov test (two-tailed test), have shoved that the difference between empirical and theoretical cumulative log normal distributions is not significant at 95% significance level (Figure 3).

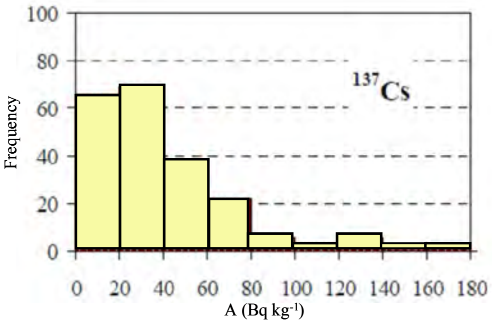

Figure 3. Frequency distribution of ^{137}Cs

However, variations in the ^{137}Cs specific activity between statistical regions were observed. ANOVA test of the log-transformed data showed that mean values among regions are different (p=0.04). The mean values and 95% LSD intervals for all regions are presented on Figure 4. The Fisher's LSD showed that the mean values of ^{137}Cs in the Southwest and the Polog region are significantly higher than the values found for other regions (LSD, $p<0.01$), which could be related to the higher quantities of rainfall in the Western part of the country compared to the East part (9).

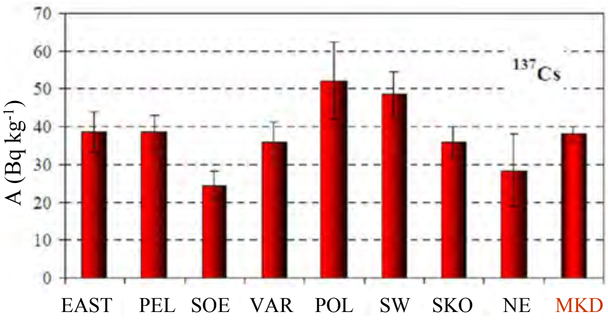

Figure 4. Mean value of ^{137}Cs specific activity in different statistical regions

Finally, the mean values for all regions as well as for the entire country area was in good agreement with the ^{137}Cs levels reported in past few years for some other neighbouring countries and countries in the region (Table 2)

Table 2. The comparison of the ^{137}Cs specific activity in soil samples from the present study with the values obtained in other studies

	A (Bq kg^{-1})		References
	Mean value	Range	
Giresum, Turkey	249	41-1305	(2)
Adana, Turkey	6.8	0.1-28	(10)
Kastamony, Turkey	8.02	0.75-16.94	(11)
Republika Srpska	26	2.1-68	(12)
Srbia	48.3	5.25-112	(13)
Kosovo	53	< 607	(14)
Republic of Macedonia	27	0.23-178	Present study

The prediction map of the ^{137}Cs specific activity, in soil through the whole country is shown in Figure 5, on which it is evident that the radionuclide has a distinct geographical distribution. It also shows a geographical trend, with high concentration in the East-West directions

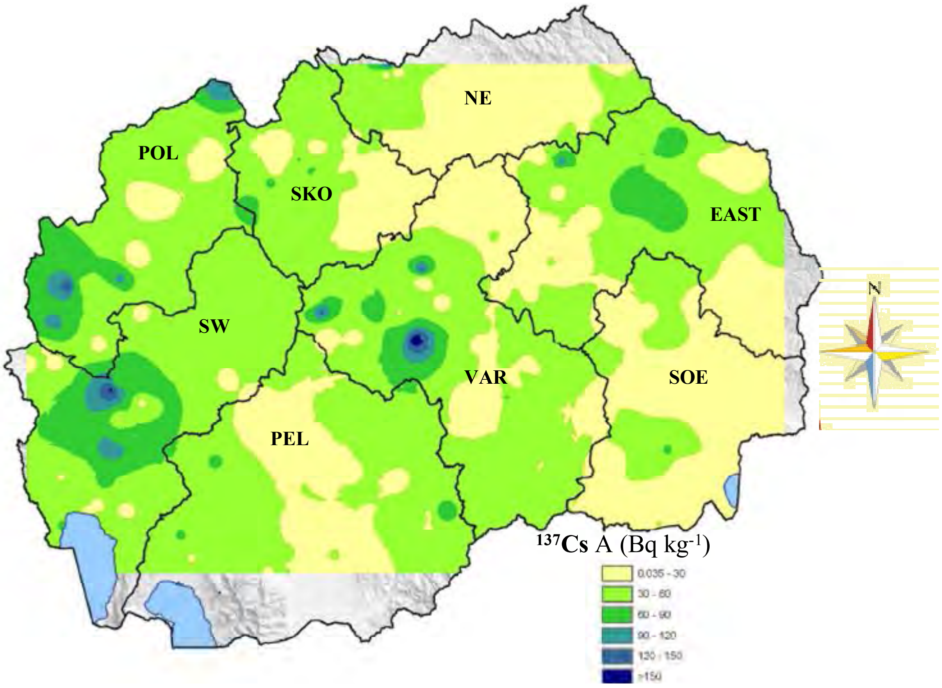

Figure 5. Interpolated map of ^{137}Cs

For further elucidation the correlation between log-transformed ^{137}Cs specific activity and the topographical variables: elevation, latitude, longitude was investigated. The Spearman correlation coefficient was determined as a measure of the linear dependence. The results shows statistically significant correlations of ^{137}Cs specific activity ($p<0.05$) with the elevation and longitude.

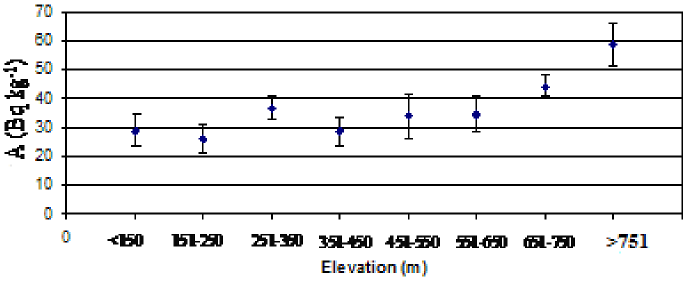

Figure 6. Specific activity of ^{137}Cs versus elevation

The higher correlation coefficient R=0.303 was found between the ^{137}Cs activity and the elevation, which is obviously when interpolated map of ^{137}Cs (Figure 5) with topological map (Figure 1) were compared. The elevation intervals which were used for differentiation into subgroups were defined to be (651-750) m and (>751) m

The lower - negative correlation appeared for ^{137}Cs versus longitude, R= -0.257. The results of the mean specific activity for different longitude are presented on Figure 6.

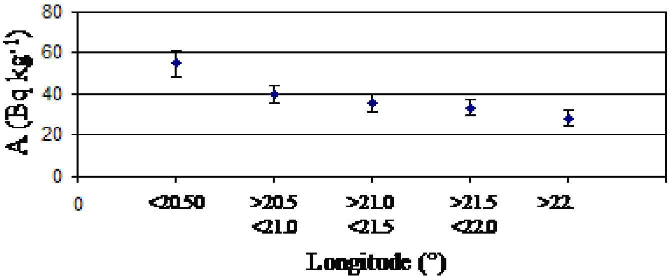

Figure 6. Specific activity of ^{137}Cs versus of longitude

5. SUMMARY

The Results of the gamma spectrometry measurements on the territory of the Republic of Macedonia revealed presence of ^{137}Cs in all surface soils samples. In general, the values are comparable with those reported in last decade from the other neighboring countries and countries from the region. The specific activity of the ^{137}Cs was found to be variable with statistical significance for the different regions (higher concentrations are found in regions with more rainfalls). The Cs-137 activity was also correlated with the elevation and longitude of the area.

The results obtained in this study may be used for estimation of population exposure to ^{137}Cs present in the environment as well as for quantitative information on patterns of erosion and sedimentation of soil (14).

6. REFERENCES

(1.) UNSCEAR, 1982. Ionizing radiation sources and biological effect. United Nations Scientific Committee on the Effect of Atomic Radiation, United Nations, New York

(2.) Celik, N., Cevik, U., Celik A., Kucukomeroglu B., 2008. Determination of indoor radon and soil radioactivity levels in Giresun, Turkey. Jurnal of Environmental Radioactivity 99(8), 1349-1354.

(3.) Andrello, C. A., Appoloni, C. R., Araujo E. S., Thomaz E. L., Medeiros P. H. A., Macedo I. L.. 2009. Cesium-137 inventories in andisturbed areas in different regions of Brazil. International Nuclear Atlantic Conference - INAC 2009. Rio de Janeiro,RJ, Brazil, September27 to October 2, 2009

(4.) Al-Hamarneh F.Ibrahim, Awadallah I. Mohammad. 2009. Soil radioactivity levels and radiation hazard assessment in the highlands of northern Jordan. Radiation Measurements 44, 102-110.

(5.) Atlas of caesium deposition on Europe after the Chernobyl accident in 1998.European Commission, ISBN 92-828-3140-X.

(6.) Државен завод за статистика, 2009. Македонија во бројки 2009. Државен завод за статистика на РМ.

(7.) ISO 18589-2, 2007. Measurement of radioactivity in the environment-Soil-Guidance for the selection of the sampling strategy, sampling and pre-treatment of samples.

(8.) ISO 18589-3, 2007. Measurement of radioactivity in the environment-Soil-Measurement of gamma-emitting radionuclides.

(9.) Zikov, M., 1995. Klima i klimatska regionalizacija vo Republika Makedonija, Geografski razgledi, kniga 30, Sojuz na geografskite zdru`enija na Republika Makedonija, Skopje.

(10.) Degerlier, M., Karahan G., and Ozger, G. 2007. Radioactivity concentrations and dose assessment for soil samples around Adana, Turkey. Jurnal of Environmental Radioactivity 99(7), 1018-1025

(11.) Kam, E., and Bozkurt, A., 2007. Environmental radioactivity measurements in Kastamonu region of northern Turkey. Applied Radiation and Isotopes 65(4), 440-444.

(12.) Janković, M., Todorović, D., and Savanović, M., 2008. Radioactivity measurements in soil samples collected in the Republic of Srpska Radiation Measurements 43(8), 1448-1452.

(13.) Dragovic, S., Onjia, A., 2006. Classification of soil samples according to geographic origin using gamma-ray spectrometry and pattern recognition methods. Applied Radiation and isotopes 65(2), 218-224.

(14.) Uyttenhove J, Lemmens M, Zizi M. 2002. Depleted uranium in Kosovo: results of a survey by gamma spectrometry on soil samples. Health Phys. 83(4):543-548.

(15.) Ritchie, J.C., McHenry J.R. 1990. Aplication of radioactive fallout Cesium – 137 for measuring soil erosion and sediment accumulation rates and patterns: A Reviev. Journal of Environmental Quality (19), 215-233.

RISK ASSESSMENT OF TAILINGS FACILITY DAM FAILURE

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Abstract: This paper presents the consequences of tailings facility dam failure and therefore the needs for its risk assessment.

Tailings are fine-grained wastes of the mining industry, output as slurries, due to mixing with water during mineral processing. Tailings dams vary a lot as it is affected by: tailings characteristics and mill output, site characteristics as: topography, hydrology, geology, groundwater, seismicity and available material and disposal methods.

The tailings which accumulates a large amount of crushed material mixed with chemically contaminated water a technological necessity, but a real danger to the environment. On the other hand the need for rehabilitation of the tailings increases the costs of the company. Much of the mining companies have closed due to unsafe working conditions, largely due to the tailings problems.

Introduction

There are three methods for building the tailing dams which depends of the geological features on the ground and soil mechanics (figure 1).

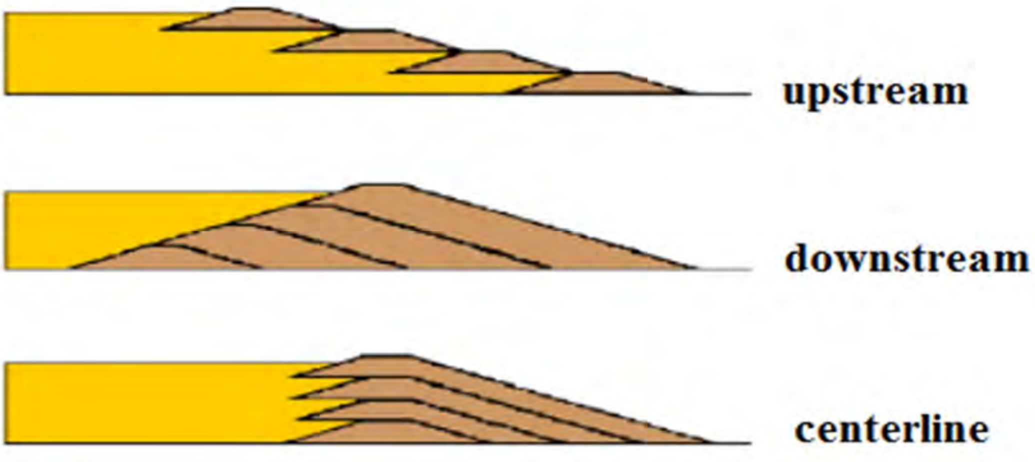


Fig. 1. Tailing dams types

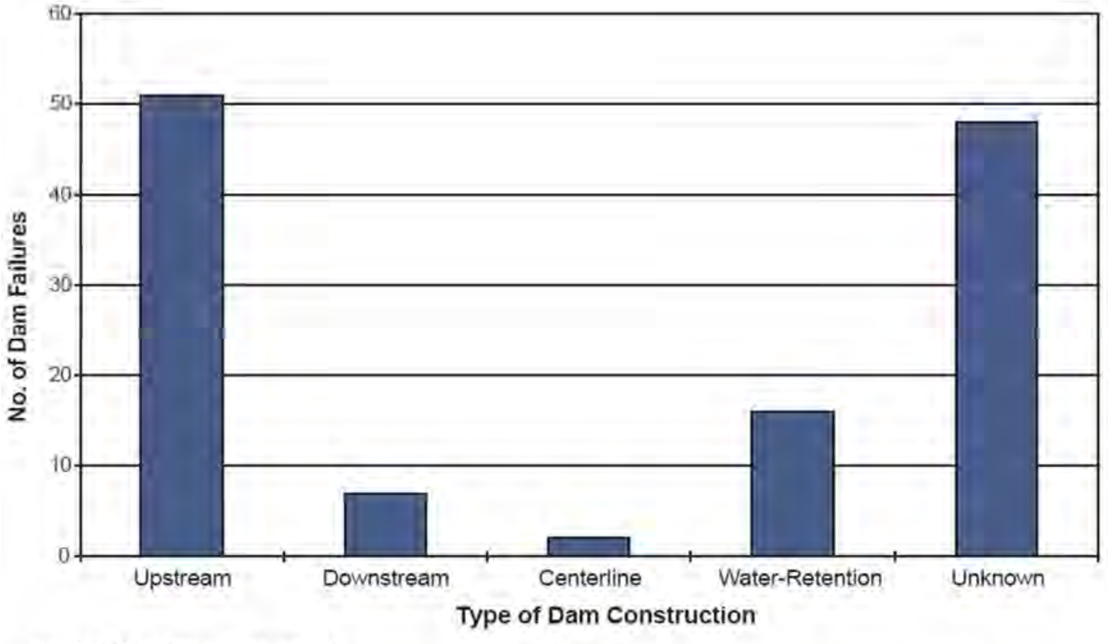
The safety for different types:

- The upstream construction method, while available at low cost, implies a number of specific hazards for dam stability. These hazards require a thorough assessment and continuous monitoring and control during siting, construction, and operation of the dam.
- Downstream-type and water-retention type embankments provide for better safety margins for dam stability.
- Another option for a safer tailings management is paste disposal rather than slurry disposal (Nilsson, 2001).

The tailings have negative environmental impacts on the environmental safety, land productivity and on the aesthetics.

Tailings dam failures by dam type

The figure 2 shown a tailings dam failures by dam type.



(USCOLD. 1994: UNEP. 1996)

Fig. 2. Tailings dam failures by dam type

Serious hazards posed by failing tailings facilities include:
- floods and flood waves
- spills of sometimes toxic sludge and waters
- spills of sludge and rubble, burying houses or settlements and their inhabitants or destroying cropland
- contaminant spills into the environment (e.g. cyanide)
- pollution of rivers and their flood banks
- poisoning of aquatic life including massive fish kills. (Meggyes et al., 2003)

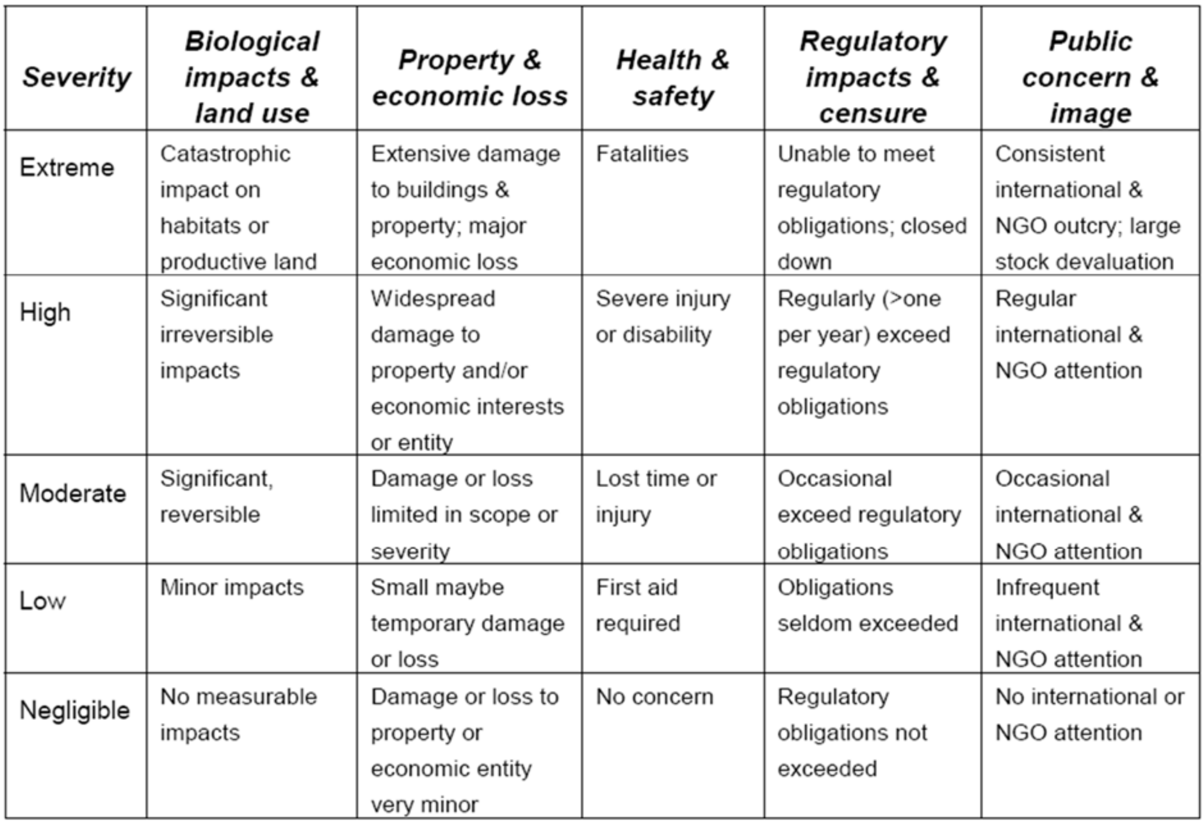
Fig. 3. Outpouring of slag as a result of tailings dam failure

Hazards arising from the possibility of tailings dam failure

- The first one is land contamination and groundwater pollution as a product of minerals extraction and direct emission of contaminants from the pond.
- The occurring phenomena and the risk presented in terms of damage to the ecosystem can be managed by the common source-pathway-target frameworks used to quantify the harm posed by contaminated land.
- The main contaminants are radioactivity, remnant cyanide and formation of acid seepage.
- The second type of hazard is the failure of tailings dams, which are traditionally constructed of tailings using the upstream method.
- Dam failure happens suddenly or within a short period, often with little warning.
- The well known effects are flood, slurry and mudflow that move downslope.
- The typical modes of failure are affected by different causes such as dam overtopping, seismic impacts, landslides within the valley of the basin or structural dam failure due to instability and unexpected seepage forces. (Meggyes et al., 2003).

In table 1 are shown the categories of severity of effects and consequences.

Table 1. Categories of severity of effects and consequences



Severity	***Biological impacts & land use***	***Property & economic loss***	***Health & safety***	***Regulatory impacts & censure***	***Public concern & image***
Extreme	Catastrophic impact on habitats or productive land	Extensive damage to buildings & property; major economic loss	Fatalities	Unable to meet regulatory obligations; closed down	Consistent international & NGO outcry; large stock devaluation
High	Significant irreversible impacts	Widespread damage to property and/or economic interests or entity	Severe injury or disability	Regularly (>one per year) exceed regulatory obligations	Regular international & NGO attention
Moderate	Significant, reversible	Damage or loss limited in scope or severity	Lost time or injury	Occasional exceed regulatory obligations	Occasional international & NGO attention
Low	Minor impacts	Small maybe temporary damage or loss	First aid required	Obligations seldom exceeded	Infrequent international & NGO attention
Negligible	No measurable impacts	Damage or loss to property or economic entity very minor	No concern	Regulatory obligations not exceeded	No international or NGO attention

Dam safety management of tailings facility

Dam safety management of tailings facility covers the procedures shown in figure 4.

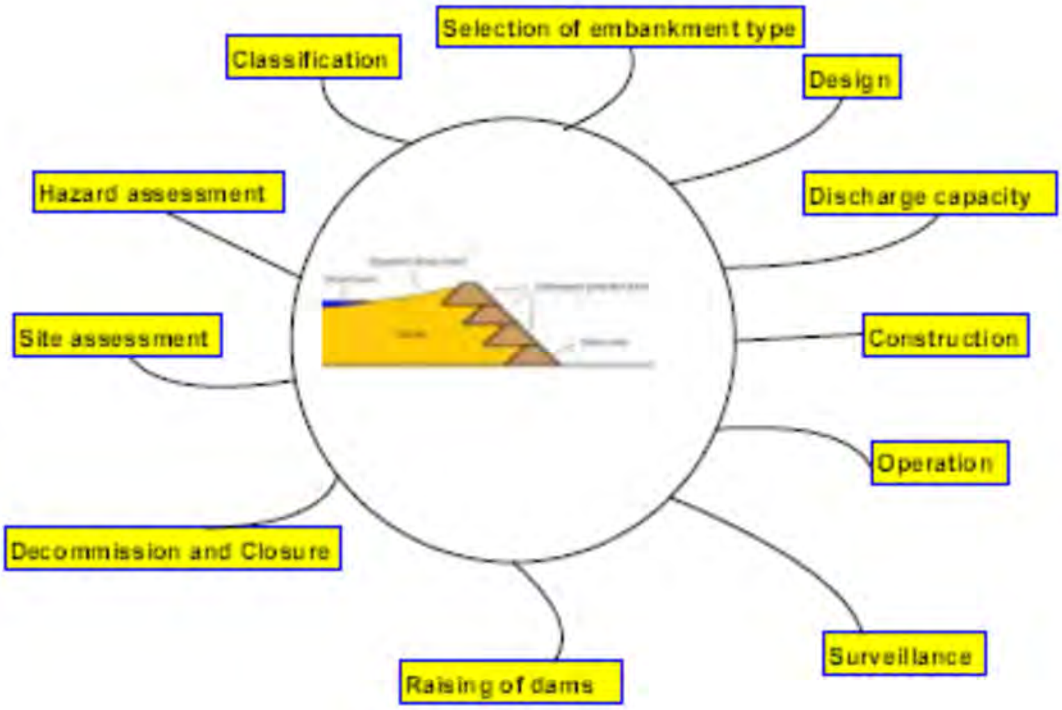


Fig. 4. The procedures of tailing dams safety management

Risk assessment stages

The risk assessment stages are given below at Figure 5.

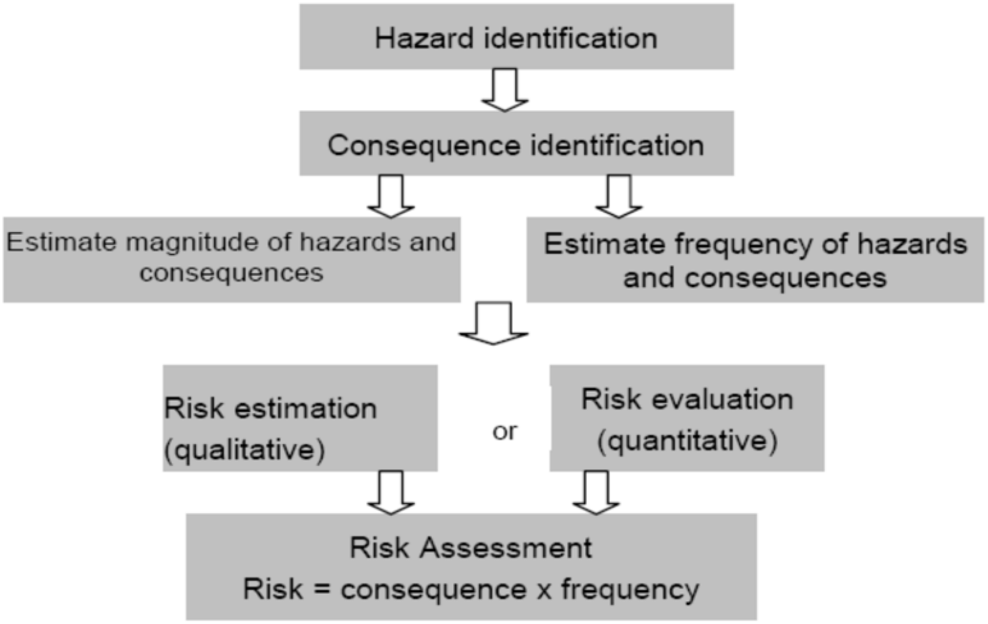


Fig. 5. Risk assessment stages

Scope and purpose of risk assessment is to determine and identify all stakeholders in the risk assessment.

Risk assessment is a structured methodology aimed at:

- Identifying the hazardous substances inventory

- Identifying possible accidents
- Estimating the Frequency of each Event
- Defining the causes for each event
- Estimating the frequencies of each scenario
- Assessing the magnitude of the consequences of each scenario

Risk assessment methodologies:

- Qualitative analysis (HAZard Operability Study)
- Quantitative analysis (CPQRA – Chemical Process Quantitative Risk Analysis)

Qualitative risk analysis

• **Preliminary Hazard Analysis (PHA),** was developed according to military standards in this field, and can be applied in the preliminary project phases. It focuses on the main areas that might contain dangerous substances, and on the main equipments, and monitors the possible failure points where dangerous substances or energies could be released.

• **"What If?"** method, poses a series of questions in order to determine unexpected events in the system.

• **Checklists** identify known and predictable risks using standards. Some of the more relevant techniques are: DSF – Diagnosis Safety Form, DCT – Diagnostique et Conditions de Travail, SDQ – Safety Diagnosis Questionnaire.

• **Hazard and Operability studies (HAZOP),** is designed to identify safety and operability problems using a systematic and structured approach by a multidisciplinary team. Using brainstorming and certain keywords deviations in the process from the normal functioning are identified, their causes and consequences on the process, humans and environment are evaluated qualitatively. HAZOP is one of the most used methods in technological hazard evaluation.

• **Failure Modes and Effects Analysis (FMEA)** determines how the failures of certain system components affect the optimum system performance. This ensures that proper safety measures are taken and safety systems are installed. The FMEA is a complementary analysis of Layer Of Protection Analysis (LOPA).

The qualitative methods focus mainly on identifying the possible hazards and express the level of risk as low-L, medium-M, high-H and extreme-E.

Likelihood	Consequences				
	Insignificant	Minor	Moderate	Major	Severe
Almost certain	M	H	H	E	E
Likely	M	M	H	H	E
Possible	L	M	M	H	E
Unlikely	L	M	M	M	H
Rare	L	L	M	M	H

Fig. 6. Qualitative risk analysis

Risk management

Risk assessment provides a basis for the development of risk management (figure 7):

– communication,

- contingency,
- mitigation and
- emergency response plans.

Fig. 7. Development of risk management

Risk management goals are:

- minimize the likelihood of adverse safety or environmental impacts;
- detect and respond to potential failures;
- establish contingency and emergency preparedness plans to deal with significant events. (The Mining Association of Canada, 1998).

Hazard assessment methodology for tailing dams

The hazard associated to a dam is appreciated by the RB index:

$$RB = CA/(a * BA + b * CB)$$

in which the weight coefficients a and b have the values:

$a = 1$ for dams and deposits that have been established according to the current provisions;
$a = 0.8$ for dams and deposits that have been established based on older regulations;
$a = 0.4$ for situations in which there is a lack of adequate data regarding the project;
$b = 1$ for dams or deposits that have had no problems during or since construction;
$b = 0.7$ for dams or deposits that had incidents or accidents during or since construction, resolved through supplementary works.

The BA index the dam's or deposit's characteristics (dimensions, type, discharge, importance class), it's location (the nature of the ground and seismicity), and the condition of the lake or waste deposit;

The CB index is determined by the situation of the dam, the sophistication of the operational controls and monitoring system(s), the level of maintenance, the dam's behaviour over time, the conditions of the accumulation lake, and the level of site-specific knowledge; and

The CA index quantifies the consequences of damage to the dam/deposit, taking into consideration: the possibility of loss of lives, potential effects on the environment, potential social-economical effects, etc. (Mara et al., 2007)

Depending on the value of the RB index, the dams are assigned to one of four hazard categories (A, B, C, or D):

RB>0.8 a dam of exceptional importance (A)
0.8 ≥RB >0.15 a dam of special importance (B)
0.15 ≥RB >0.05 a dam of normal importance (C)
RB ≤ 0.05 a dam of low importance (D)

The importance of risk assessment

- Risk assessment helps to focus on cost effective approaches to improving the performance of tailing systems.
- Depending on the available data, risk assessment can be carried out in a more or less quantitative manner, starting from a qualitative identification of possible hazards to a quantitative risk evaluation concerning the probabilities of failure and its economic consequences.
- Risk assessment needs to occur before and during an operation, and must also address closure issues, particularly since tailings dams outlast mines and their stability has to be guaranteed "in perpetuity".
- Risk management is an ongoing process rather than a one-off activity.
- Risk assessment may not cover well, some very low-probability/high consequence events, such as those which characterize certain tailings failures.

Conclusion

Actions to reduce risk:

- Improving quality control;
- Documenting construction and quality control by more use of as-built records;
- Improving construction procedures consistent with recommendations from well-qualified geotechnical engineers familiar with the mining industry;
- Utilizing more third party reviews;
- Ensuring that there is no conflict between short term profitability and long term integrity of containment;
- Ensuring that the responsibility for failure of waste containment structures is understood at the highest corporate levels and that the standard of care is set by senior mine management (Morgenstern, 2001).

References

Alexandru Ozunu, Institutional Practitioner Training in Risk Management in Mining 7-11 December 2009, Tirana, Albania

Bruce, Iain G., Logue, Clint, Wilchek, Lori-Ann , 1997, Trends in Tailing Dam Safety

Hartford, D.N.D., 1998, Risk assessment in environmental risk management of tailings dams, in ICME/UNEP Workshop on Risk Assessment and Contingency Planning in the Management on Mine Tailings, Argentina

Meggyes, Tamás, McDonald, Chris, Roehl, Karl Ernst, Witt, Karl Josef, Debreczeni, Ákos, Niederleithinger, Ernst, 2003, Reducing the risk for tailings facilities, Proceedings of Consoil

Morgenster, Norbert, 2001, Geotechnics and mine waste management – update, Seminar on safe tailings dam constructions, Technical Papers

Nilsson, Åke, 2001, Safe dam constructions, Seminar on Safe Tailings Dam Constructions, Technical Papers

The World Bank Environmentally and Socially Sustainable Development Unit, 2003, Romania Hazard and Risk Mitigation and Emergency Preparedness Project: Setting Priorities for the Mining Sector

The Mining Association of Canada, 1998, A Guide to the Management of Tailings Facilities

HYDROGEOCHEMICAL ANALYSIS OF WATERS FROM ZDRAVEVCI-BOROVIĆ GEOTHERMAL SYSTEM IN NE MACEDONIA

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Abstract

In the paper, the water properties of the geothermal system Zdravevci-Borović are discussed. Several well have been drilled in the valley of river Povišnica in the Kratovo-Zletovo area, with temperatures up to 50ºC and artesian flow of about Q=10 l/s. Geochemical analysis of waters shows that waters belong to Ca-HCO_3-SO_4 and other types and are meteoric in origin (based on isotope analyses). Water is therefore infiltrated through sedimentary and volcanic rocks through fractures, is heated due to presence of magmatic pluton and naturally outflows through the fractures in wells at the surface. From geochemical modeling, it is expected that several iron hydroxides and oxides can precipitate on the surface, and this precipitation is confirmed in the field. Although some of ion concentrations are above drinking water limits, geothermal potential for exploitation remains, with proper treatment of water. Further systematic geochemical sampling and hydrogeological testing of the wells is recommended for deeper understanding of this geothermal system.

Key words: Borović, hydrogeochemistry, wells, geothermal water, Macedonia

Introduction

Geothermal potential in Republic of Macedonia is very large. Many of such areas are already in use, with major ones being Kočani geothermal field, Vinica and Gevgelija. Water is used mostly for agriculture, greenhouse heating and balneology (Donevski, 2008). However, several other remain unexploited, as at least 32 geothermal locations are known with temperatures up to 150 ºC. One of practically unexploited area is the location Borović in geothermal system Zdravevci in NE Macedonia. The purpose of the paper is to present the hydrogeochemical properties of the geothermal water in this area.

Geology of the studied area

Studied area lies below the Borović hill (651 m), few kilometers west from town of Kratovo in NE Macedonia (42.07ºN, 22.08 ºE). The nearest villages are Topolović and Turalevo in the north and Filipovci in the south. Area belongs to Zdravevci geothermal system, named after a nearby smaller village. The region is also known as Borović (or Borovik, originally Боровиќ) ore field, and is therefore noted further on in the paper as

Zdravevci-Borović geothermal system. Borović is one of the volcanic manifestations in the wider Kratovo-Zletovo volcanic area, and several wells were drilled in the valley of river Povišnica (Povišica) in late 1980's.

Kratovo-Zletovo area lies in a former volcanic crater or caldera (Turalevo crater), which was later significantly altered by intensive hydrothermal alternation, silicification (up to 99% SiO_2), jarositization and kaolinitization. The area was intensively studied for the occurrence of ore minerals, and high values of Pb, Zn and Cu were found. Area was mostly studied by (Klajn, 1977) and (Rakić et al., 1993).

In the area of Zdravevci-Borović system, the oldest and deepest rocks are Paleozoic and Precambrian magmatic and metamorphic rocks (schists and amphibolitic rocks) of Serbo-Macedonian mass, and granodioritic pluton bodies (Klajn, 1977; Rakić et al., 1995; Rakić et al., 1993; Tasev, 2010). Estimated temperature in this source is about 200 ºC. These rocks are covered by Eocene and Oligocene sedimentary, volcanic and sedimentary-volcanic rocks, mostly clastic rocks and flysch (Figure 1), plus volcanic intrusions of dacite-andesite and diorite. Conglomerate and breccia prevail in Eocene and Middle Oligocene is represented by sandstones, breccias and limestones with high amount of volcanic material. Miocene is composed of various sandstones, marls and tuffs, Pliocene mostly by clastic rocks, and Quaternary by alluvium and delluvium. All these rocks are dissected by andesitic and dacitic eruptive rocks, tuffs and ignimbrites. Complete thickness of rocks above the pluton is about 1000-2000 m (Mičevski et al., 2007).

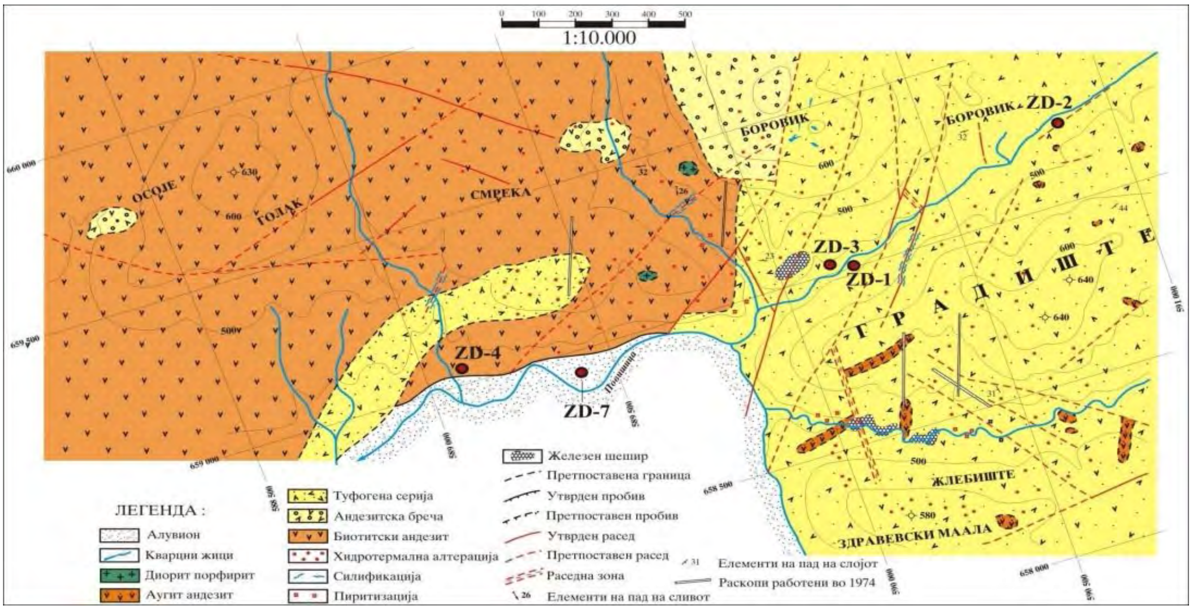

Figure 1. Modified geological map of Zdravevci-Borović area with locations of wells (modified after Klajn, 1977).

Wells (figure 1) were drilled to various depths: well ZD-1 to 90 m, ZD-2: 107 m, ZD-3: 335 m, ZD-4: 134 m, ZD-5: 129 m, ZD-6: 96 m and later wells ZD-7 and ZD-9 (depths unknown). The major borehole ZD-3 lies 444 m above sea level in the valley of Povišnica and was drilled in 1989. Borehole diameter is 86 mm with installed casing of 3,5 inches. The well is drilled in a fracture zone and is relatively deeper than other surrounding boreholes.

Water was recognized early in 1991 as therapeutic (Milenković, 1991). Water is artesian and flows from the well ZD-3 with approximate discharge of Q = 10–11 l/s. The temperature of the water varies with depth and due to interaction with surface water and lies in the range of 43-48 ºC. Maximum temperature in the well was 50,8 ºC. Two aquifers have been found to exist in the area, first in the depth of 83 m and second on 210 m (Đuzelovski, 1999).

Methods and materials

Waters were sampled in two periods, first on 22.06.1991 and later in summer 2005. In the first period, only the major well ZD-3 was sampled, with intention to check the possibility of water for therapeutic use (Milenković, 1991). Second sampling was done in 2005, and water samples from three wells ZD-3, ZD-7 and ZD-9 (Figure 2) were analyzed for geochemical composition and isotopes, plus the river Povišnica. Note that the results from the 2005 analysis for the well ZD-3 are not presented in this study, as sulphate concentration was far too low from expected and also far too low from the previous analysis in 1991, so this analysis was omitted.

Figure 2. Natural discharge of the well in Zdravevci-Borović area. Note the lack of vegetation in the background due to hydrothermal alteration and iron mineral precipitates in the creek bed in the foreground.

Analyses from the year 1991 were performed in laboratory in Belgrade, Serbia and analyses in 2005 in the ActLab laboratory in Canada. Measurements of water temperature and pH were determined in the field. Isotope composition of δD and $\delta^{18}O$ was performed in Ljubljana, Slovenia. As the concentration of HCO_3 ion (for the 2005 analyses) was not performed, it was calculated as the missing ion in geochemical software AquaChem via calculation of electrical balance to achieve electroneutrality. Saturation indices were calculated by software PHREEQC for Windows.

Results and discussion

Waters from wells belong to Ca-Na-HCO_3-SO_4, Na-Ca-HCO_3-SO_4 and Ca-HCO_3-SO_4 types and therefore their origin can be attributed to carbonates-sulphates with elevated Na values from volcanic complex, reflecting the groundwater composition. From the isotope data it is clear that although deviations from the Meteoric Water Line (MWL) $\delta D = 8 \times \delta^{18}O + 10$ occur (Figure 3), samples are still grouped along this line. Water is therefore believed to be infiltrated meteoric water, which infiltrates through several fractures in sedimentary and volcanic rocks, is progressively heated in the depth and is later captured in the wells near the surface.

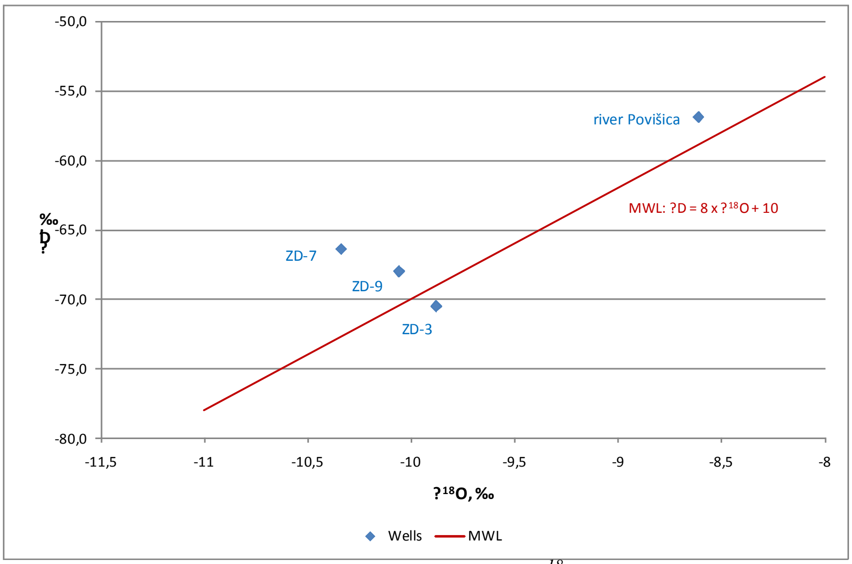

Figure 3. Isotope composition of Zdravevci-Borović wells ($\delta^{18}O$ and δD).MWL: Meteoric Water Line.

Water is highly mineralized, as the total dissolved solids value (TDS) is 3458 mg/l (based on the 1991 analysis). Water composition is presented on the Piper and Schoeller plots (Figure 4), and water from all wells belongs to one group.

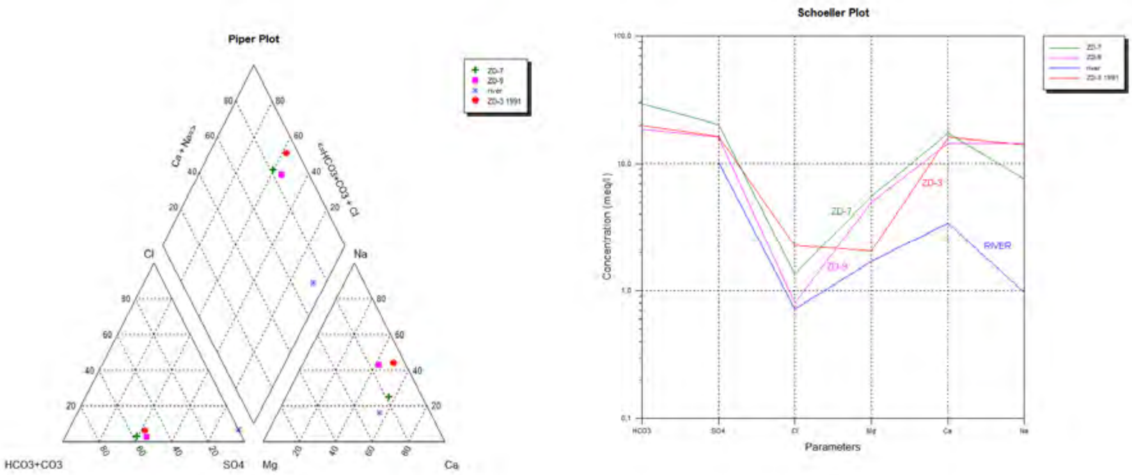

Figure 4. Piper and Schoeller plots of hydrogeochemical analyses of Zdravevci-Borović waters.

Temperature from deepest well ZD-3 was 43-44 ºC, but significantly lower in other two wells (21,2 ºC in well ZD-7 and 22,8 ºC in ZD-9). The reason for relatively cooler water can be attributed to lower well depth of two wells, as infiltrated water is progressively heated in greater depths. Deeper well ZD-3 is also situated in a more fractured zone, which permits higher circulation rate of water. Obviously, the potential for geothermal exploitation of the area exists, as the water outflows naturally from the wells (Figure 2). If pumped, the cooling effects would be less pronounced and temperature would be higher on the surface.

Table 1. Selected concentration of water wells and river Povišnica and saturation indices of calcite, gypsum, goethite and hematite. Bold numbers indicate exceeded drinking water limit values.

Well	pH	Na	Fe	Mn	Ni	As	Cu	Pb	Zn	Br	F	SO4	SI$_{cal}$	SI$_{gyp}$	SI$_{goe}$	SI$_{hem}$
unit	-	*mg/l*	*mg/l*	*µg/l*	*µg/l*	*µg/l*	*µg/l*	*µg/l*	*µg/l*	*µg/l*	*mg/l*	*mg/l*	-	-	-	-
river	**5,7**	22,4	0,19	**50,1**	5,7	1,73	**3,7**	2,25	24,1	26	0,3	**488**	-	-	-	-
ZD-3 1991	6,5	**324,5**	**0,90**	**300**	5	**40**	**5**	5	30	0	**1,8**	**780**	0,52	-0,53	6,97	16,02
ZD-7	**5,8**	173	**5,15**	**872**	**25,1**	**49,6**	**4,0**	0,72	9,8	**131**	**1,8**	**971**	-0,29	-0,44	4,37	10,72
ZD-9	**6,0**	**333**	**3,93**	**350**	**69,2**	**60,6**	**8,4**	0,43	7,7	**145**	0,8	**767**	-0,30	-0,56	5,05	12,11
limit	*6,5-9,5*	*200*	*0,2*	*50*	*20*	*10*	*2*	*10*	-	*10*	*1,5*	*250*	-	-	-	-

Despite the location in the regional area of highly mineralized ore deposits with Pb-Zn and Cu, and the fact that such surface waters can be highly contaminated with metals like Cu and Zn values for the the waters in Kratovo-Zletovo area (Alderton et al., 2005), the analyzed waters do not show exceeded values of permissible drinking water element concentrations for Pb or Zn. However, several other metals and parameters are exceeded (Table 1) in regard to EU Drinking Water Directive (98/83/EC). Values of Fe, Mn and SO_4 are greatly exceeded in all wells, and some other parameters also exceed the permissible limits for Cu, Na, Ni, As, Cu and F. The pH values are also a bit lower than lower limit. Selected calculated saturation indices (Table 1) indicate that the water is greatly oversaturated by iron oxides and hydroxides (SI>10), and slightly undersaturated or in relative equilibrium with calcite and gypsum (SI is around ±0,5). Iron minerals are therefore expected to precipitate from the water, and such precipitates are indeed visible in the field (Figure 2).

Conclusions

The investigated area of Zdravevci-Borović geothermal system is potentially interesting for geothermal water exploration and exploitation, as water from wells has temperatures up to about 50ºC, with discharge of approximately 10 l/s. With the use of submersible pumps, even higher temperatures at higher discharges can be obtained.

Several of analyzed parameters (especially Fe, Mn and SO_4) are above the critical value for drinking water. The water has been however recognized as theraupeutic (in 1991), so potential for exploitation remains if treatment of water can be introduced.

Origin of water can be related to sedimentary (carbonate) and volcanic cover due to its geochemical composition, and the water is attributed to be meteoric (shown by isotopes). Water infiltrates in fractured rocks, is progressively heated in the depth and captured at the surface at relatively high temperatures (highest in well ZD-3).

By further isotope analyses (tritium), the age of water and cycling could be determined. Systematic geochemical sampling of water from wells should be performed in the future to get further information on the water-rock interaction, to study the speciation and mobility of elements and evolution of ground water. The wells should be hydraulically tested for influence to determine the effects of pumping on temperature and discharge.

References

Alderton, D.H.M., Serafimovski, T., Mullen, B., Fairall, K., James, S., 2005. The Chemistry of Waters Associated with Metal Mining in Macedonia. Mine Water and the Environment, 24: 139-149.

Donevski, B., 2008. Energy Sector in Macedonia: Current Status and Plans

Sustainable Energy Technologies. In: Hanjalić, K., Krol, R., Lekić, A. (Eds.). Springer Netherlands, pp. 303-320.

Đuzelovski, D., 1999. Podzemnite vodi (izdan) za reševanje na vodosnabduvanjeto vo R. Makedonija i nivnata zaštita. Institut "Geohidroproekt", Skopje, 308 pp.

Klajn, Đ., 1977. Geološke, geohemiske i metalogenetske odlike rudnih pojava Borovika u SR Makedoniji, Institut za geološko-rudarska istraživanja i ispitivanja nuklearnih i drugih mineralnih sirovina, Beograd.

Mičevski, E., Popovski, K., Popovska-Vasilevska, S., Kolčakovski, Ž., 2007. The hydrogeothermal potential of the Vardar zone and Serbo-Macedonian mass and energetical valorization of the available geothermal resources at the territory of the Republic of Macedonia, European Geothermal Congress, Unterhaching, Germany.

Milenković, J., 1991. Kompletna fiziko-hemijska analiza mineralne vode iz istražne bušotine ZD-3 kod Kratova i stručno mišljenje o njenoj terapijskoj vrednosti, Institut za rehabilitaciju, Beograd.

Rakić, S., Đorđević, N., Stolić, N., 1995. Geotermalna potencijalnost na Kratovsko-Zletovskata vulkanska oblast. In: Popovski, K. (Ed.), Geotermalna energija: sostojba i perspektivi vo Republika Makedonija. MANU.

Rakić, S., Micevski, E., Stolić, N., 1993. Elaborat za dosegašnite geotermalni istražuvanja na terenot zapadno od Kratovo-geotermalen sistem Zdravevci so presmetka na rezervite na hidrotermalnite fluidi, Geološka služba na RIK Sileks Kratovo i Geohidroproekt, Skopje., Skopje.

Tasev, G., 2010. Metallogeny of the polymetallic ore-bearing system Bukovik-Kadiica, University "Goce Delčev", Štip, 206 pp.

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