Faculty of Sciences, Institute of Mineralogy and Petrology, University of Zagreb, R. Croatia and Croatian UNESCO-IGCP Committee with a sponsorship from the UNESCO organize

United Nations
Educational, Scientific and
Cultural Organization

2nd INTERNATIONAL WORKSHOP ON THE PROJECT

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

PROCEEDINGS

Edited by
Bermanec & Serafimovski
Zagreb, 6-7 October 2011

Faculty of Sciences, Institute of Mineralogy and Petrology,
University of Zagreb, R. Croatia and Croatian UNESCO-IGCP
Committee with a sponsorship from the UNESCO organize

2nd INTERNATIONAL WORKSHOP
ON THE PROJECT

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

PROCEEDINGS

Edited by:
V. Bermanec & T. Serafimovski
Zagreb, 6-7 October 2011

Organizing Committee:

Prof. D-r Vladimir Bermanec, *President*
Faculty of Sciences, Institute of Mineralogy and Petrology, University of Zagreb, R. Croatia

Prof. D-r Todor Serafimovski
Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

Prof. D-r Ladislav Palinkaš
Faculty of Sciences, Institute of Mineralogy and Petrology, University of Zagreb, R. Croatia

Prof. D-r Goran Kniewald
Center for Marine and Environmental Research, Rudjer Bošković Institute, Zagreb, R. Croatia

Doc. D-r Sabina Strmić-Palinkaš
Faculty of Sciences, Institute of Mineralogy and Petrology, University of Zagreb, R. Croatia

Doc. D-r Željka Žigovečki-Gobac
Faculty of Sciences, Institute of Mineralogy and Petrology, University of Zagreb, R. Croatia

Doc. D-r Marta Mileusnić
Faculty of Mining, Geology and Petroleum Engineering, Department of Mineralogy, Petrology and mineral resources, University of Zagreb, R. Croatia

Andrea Čobić, dipl.inž.
Faculty of Sciences, Institute of Mineralogy and Petrology, University of Zagreb, R. Croatia

Scientific Committee:

Prof. D-r Vladimir Bermanec, *President*
Faculty of Sciences, Institute of Mineralogy and Petrology, University of Zagreb, R. Croatia

Prof. D-r Goran Durn
Faculty of Mining, Geology and Petroleum Engineering, Department of Mineralogy, Petrology and mineral resources, University of Zagreb, R. Croatia

Prof. D-r Ivan Sondi
Faculty of Mining, Geology and Petroleum Engineering, Department of Mineralogy, Petrology and mineral resources, University of Zagreb, R. Croatia

Prof. D-r Blažo Boev
Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

Prof. D-r David H. M. Aldeton
Department of Earth Sciences, Royal Holloway University of London, United Kingdom

Prof. D-r Tadej Dolenec
Faculty of Natural Sciences and Engineering, Department of Geology, University in Ljubljana, R. Slovenia

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

C O N T E N T S

CRYSTAL MORPHOLOGY OF SANIDINE PHENOCRYSTS FROM ZVEGOR, REPUBLIC OF MACEDONIA

Tena Šijakova Ivanova[1], Andrea Čobić[2*], Željka Žigovečki Gobac[2], Vladimir Zebec[3], Vladimir Bermanec[2]

[1] *University Goce Delčev, Faculty of natural and technical science, Štip*
[2] *Faculty of Science, Institute of Mineralogy and Petrology, Zagreb, Croatia; *ancobic@geol.pmf.hr*
[3]*Croatian Natural History Museum, Zagreb, Croatia*

Abstract: This paper presents the results of the research carried out on sanidine crystals from Zvegor, Republic of Macedonia. 572 crystals were collected for research: 326 single crystals and 23 randomly intergrown crystals, 100 right-handed and 123 left-handed Carlsbad twins. Results show that left- and right-handed Carlsbad twins are almost equally represented at this locality. Goniometric measurements showed the appearance of six forms: {010}, {110}, {130}, {001}, $\{\bar{1}11\}$ and $\{\bar{2}01\}$. XRPD analysis of the sanidine - crust (Fds_C), showed that it consists of a mixture of three different phases: calcite as a dominant phase, illite and sanidine. The mixture of these phases could be a result of the feldspar crystal alteration which was primary of sanidine composition. The alteration could have been due to influence of solutions which also affected other components of the rock. It could also be a result of a post crystallization reaction of sanidine with the altered rock. XRPD analysis shows that the core of the sample (Fds_S) is sanidine.

Key words: Carlsbad twins, randomly intergrown crystals, sanidine, single crystals, Zvegor

INTRODUCTION

Zvegor is a part of Delcevo municipality in eastern Republic of Macedonia. It is 2.62 km away from the center of the municipality. There is an outcrop of quartz latite rocks which contains sanidine crystals east of the village Zvegor, close to the Macedonian-Bulgarian state border. These rocks pass through Cambrian volcanic sediments, granitoids and Paleogene formations, while Triassic sediments thrust over them and Pliocene is transgressive (Fig.1). Except sanidine, these quartz latite rocks are composed of plagioclase, quartz, amphibole and biotite. Accessory minerals are: apatite, magnetite and titanite. The rock structure is holocrystalline porphyritic. Crystals of sanidine are idiomorphic and quite rich in forms. They are usually 1 to 5 cm long. Crystals are developed as singles crystals, either loose single crystals or agglomerations of randomly intergrown crystals in a form of crystal clusters, and Carlsbad twins, both left- and right-handed. The relatively fast chemical weathering of the host rock results in a large quantity of fresh crystals that are easily released from the rock and can easily be found at the outcrops near the road. In spite of attractive crystals near the main road, they were not described, yet.

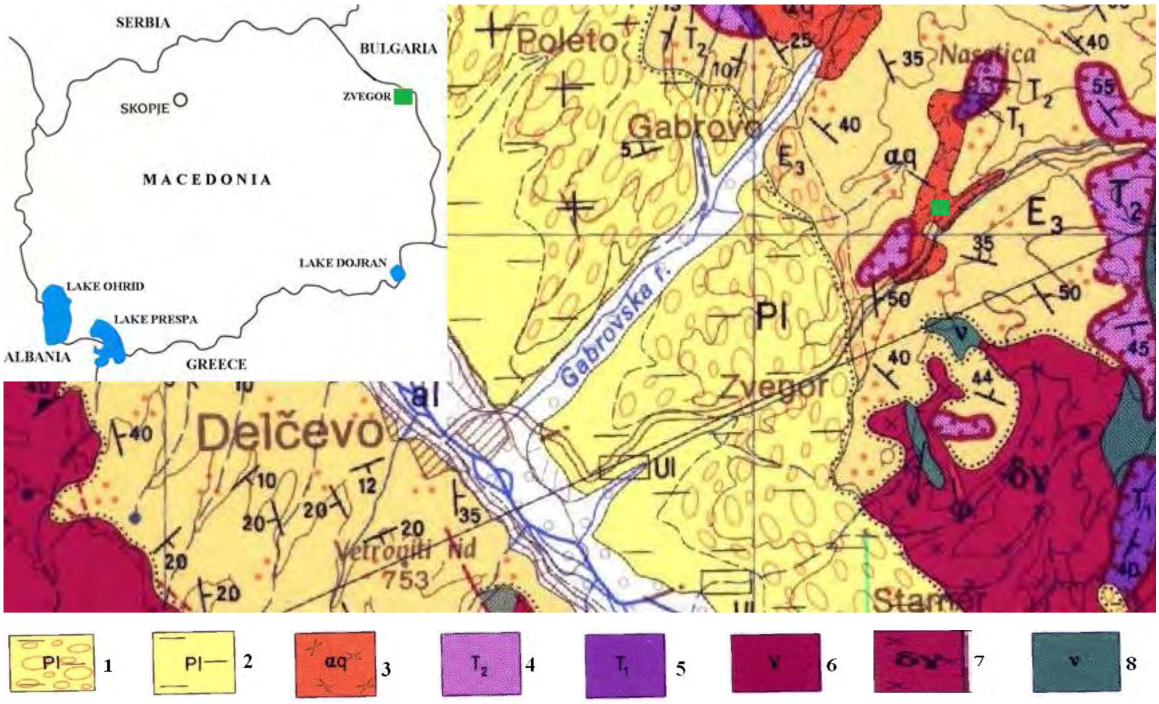


Fig. 1. Geological map of Zvegor, scale 1 : 100 000 (OGK, List Delcevo, 1981)
1. sand and gravel; 2. clay and sand; 3. quartz latite; 4. limestone; 5. sand and conglomerate; 6. aplitoide granites; 7. granodiorites; 8. metagabbro-diabase; ■ pace where the samples were taken

EXPERIMENTAL

Crystal morphology of 572 collected crystals of alkali feldspar was examined to evaluate statistical distribution of different crystal habits.

Representative twin crystal was chosen for goniometric measurements. For goniometric measurements, twocircle goniometer was used. Identification of forms was done using orientation after Goldschmidt (1897).

Representative sample was chosen for X-ray powder diffraction analysis. The crust (Fds_C) and the core (Fds_S) of the sample have been analyzed separately. X-ray powder diffraction data were collected using a Philips PW3050/60 X'Pert PRO X-ray powder diffractometer with Cu Kα radiation, accelerated by 40 kV and a current of 40 mA. Step-scan was employed in order to obtain XRPD patterns. Step size was 0.02° and counting time 1s per step. X-ray pattern analyses were performed using X'Pert High Score Plus v. 2.1 software (Panalytical, 2004) and unit cell calculations were performed using "Unit Cell" software (Holland & Redfern, 1997).

RESULTS AND DISCUSSION

The sanidine crystals are easily released from the rock which could be due to early rock alteration. Only loose crystals were collected for this study of crystal morphology. Collected crystals have been separated in two main groups which are subdivided each to two groups (Table 1). First group comprises of 349 crystals which appear as single loose crystals (326 crystals: Fig. 2a, Table 1) or agglomerations of randomly intergrown crystals (23 agglomerations; Fig. 2b, Table 1). Second group comprises of 223 Carlsbad twins, 123 left- handed (Fig. 2c, Table 1) and 100 right-handed (Fig. 2d, Table 1) which can point to the fact that they are almost equally represented at this locality. Twinned crystals developed according to the most usual twinning law for sanidine crystals - Carlsbad's law (Goldschmidt, 1916; Smith, 1974). No other twinning law was observed. When a basal pinacoid, {001}, is oriented towards the observer and the twin crystal is on the left side, it is a left-handed Carlsbad twin (Fig. 2c) and vice versa for right-handed Carlsbad twins.

Goniometric measurements have yielded six common forms: {010}, {110}, {130}, {001}, $\{\bar{1}11\}$ and $\{\bar{2}01\}$ (fig. 2). Single crystals are elongated along [100] (fig. 2a) while twinned crystals are elongated along [001] (fig. 2c-2d).

XRPD analysis of the sample-core (Fds_S), which is transparent, has confirmed a sanidine crystal structure (PDF: 01-086-0682, ICCD, 2004; Fig. 3) yielding following unit cell parameters: a = 8.512(3) Å, b = 13.024(4) Å, c = 7.181(4) Å and ß = 115.99(2) °. XRPD analysis of the crust (Fds_C), which is white, thin and readily detached, showed that it consists of a mixture of three different phases: calcite as a dominant phase, illite and sanidine (Fig. 4). The mixture of these phases could be a result of the feldspar crystal alteration which was primary of sanidine composition. Surface of sanidine phenocrysts could be altered due to influence of CO_2-rich solutions which also affected other components of the rock. It is also possible that the crust of sanidine crystals is a result of a post crystallization reaction of sanidine with the altered rock.

Table 1. List of collected samples

single crystals			Carlsbad twins			SUM
single loose crystals	agglomerations	total (%)	right-handed	left-handed	total (%)	
326	23	61	100	123	39	572

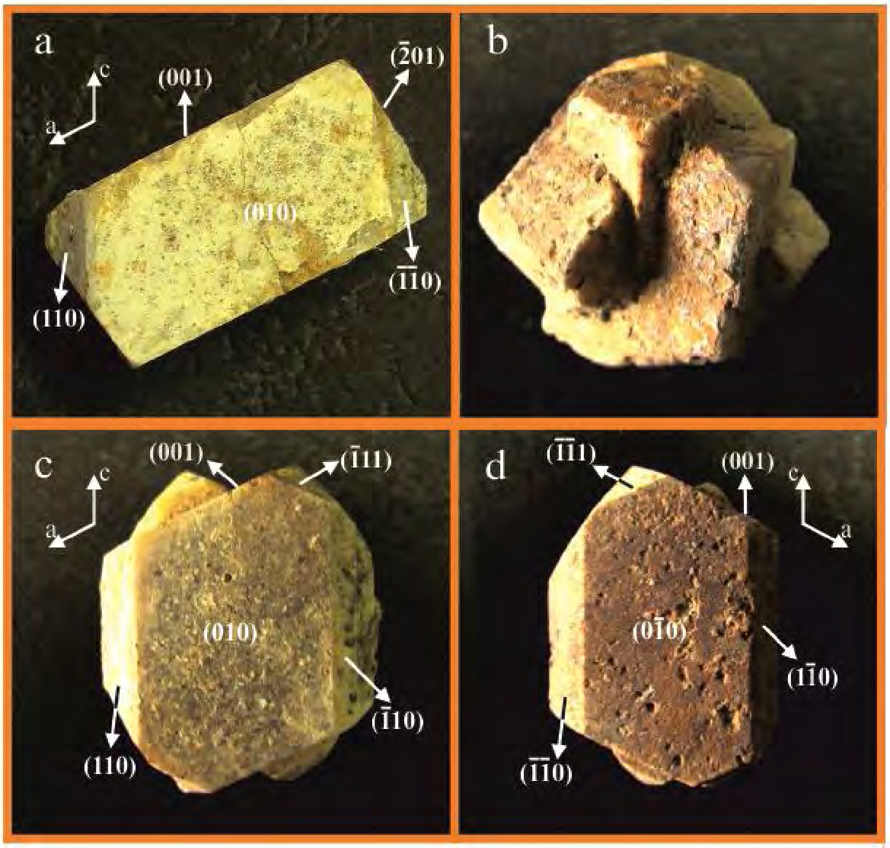


Fig. 2. Single crystals (a), agglomerations of randomly intergrown single crystals (b), Carlsbad twins: left-handed (c), right-handed (d); crystals and twins in the figure are 1 to 3 cm long

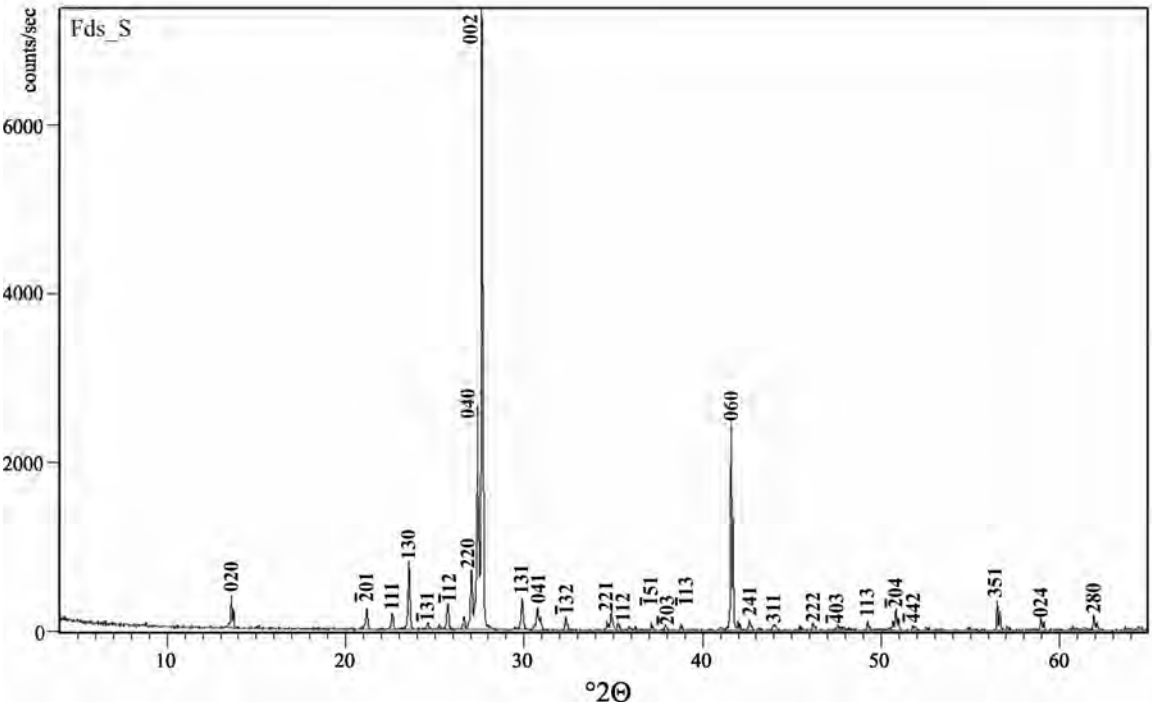


Fig. 3. X-ray diffraction pattern of sanidine sample-core from Zvegor (Fds_S).
Pattern is indexed according to PDF: 01-086-0682 (ICCD, 2004)

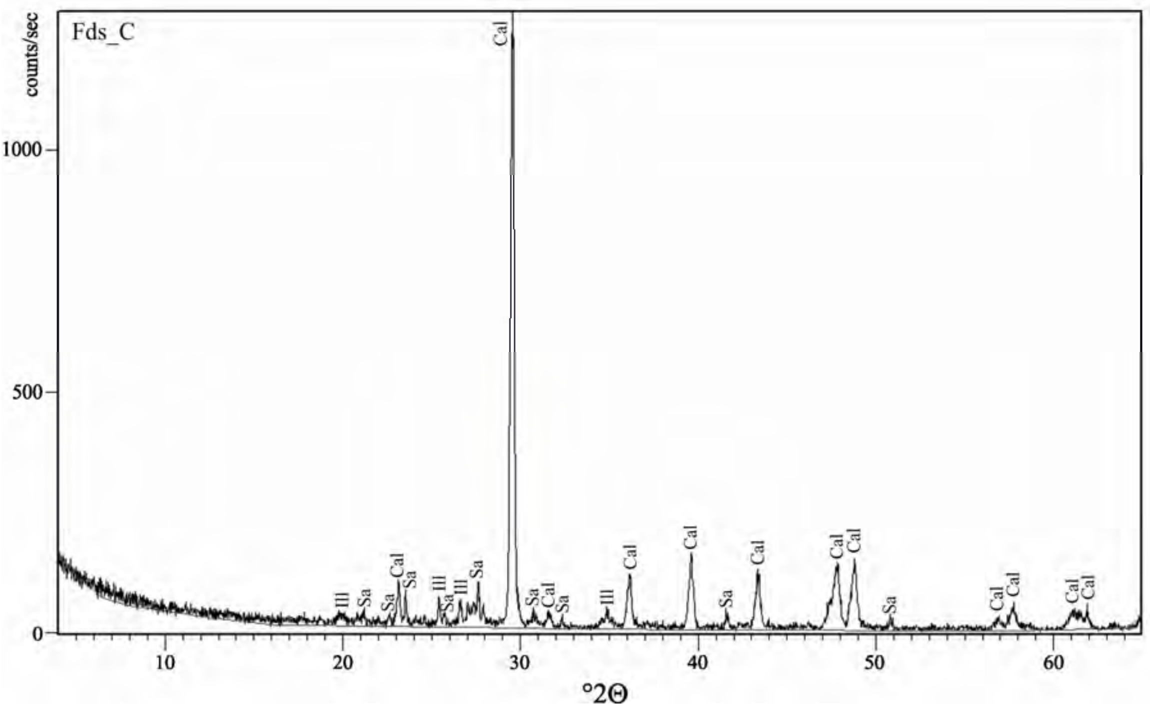


Fig. 4. X-ray diffraction pattern of sanidine sample-crust from Zvegor (Fds_C);
Cal-calcite, Ill-illite, Sa-sanidine

CONCLUSION

In general, after summarizing all the facts, which have resulted from this research it can be concluded that left- and right-handed Carlsbad twins are almost equally represented at this locality while the most frequent are single crystals of sanidine. Six forms appear on sanidine crystals: {010}, {110}, {130}, {001}, {$\bar{1}$11} and {$\bar{2}$01}. Single crystals are elongated along [100], while twinned crystals are elongated along [001] and flattened on (010).

XRPD analysis showed that the phenocrysts is sanidine and that the crust of these samples consists of a mixture of three different phases: calcite as a dominant phase, illite and sanidine. The mixture of these phases could be a result of the feldspar crystal alteration during crystallization of the rock. Surface of the phenocrysts of sanidine could be altered due to influence of CO2-rich solutions which also affected other components of the rock and caused later destruction of the volcanic rock. The other possible reason for alteration is a post crystallization reaction of sanidine with the altered rock.

REFERENCES

Goldschmidt, V. (1897): Krystallographische Winkeltabellen, Verlag von Julius Springer, Berlin, 432 p.

Goldschmidt, V. (1916): Atlas der Krystallformen, Tafeln, Band III, Carl Winters Universitätsbuchhandlung, Heidelberg

Holland, T. J. B & Redfern, S. A. T. (1997): Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineral. Mag*. **61**, 65-77

ICCD (2004): PDF-2 – Release 2004, Newton Square, U.S.A.

Kovacevik, M., Rakikevik, T., Arsovski, M., (1981) Osnovna geoloska karta 1:100 000 list, K34-82, Delcevo, Geoloski zavod Skopje, SFRJ, Belgrad

Kovacevik, M., Petkovski, P., Temkova ,V., (1981) tolkuvac na list, K34-82, Delcevo. Geoloski zavod Skopje, SFRJ, Belgrad

Panalytical (2004): X'Pert High Score Plus, version 2.1, Panalytical, Almelo, The Netherlands

Smith, J.V. (1974): Feldspar minerals 2: Chemical and Textural Properties. Springer-Verlag, Berlin, 690 p.

THE INFLUENCE OF HISTORIC MINING AND URBANIZATION ON GEOCHEMICAL AND BACTERIOLOGICAL CHARACTERISTICS OF THE GRADNA STREAM, SAMOBORSKA GORA MTS., CROATIA

Maja Kuzmanović[1], Sabina Strmić Palinkaš[1,*], Ladislav Palinkaš[1], Jasna Hrenović[2], Štefica Kampić[1], Predrag Tepeš[3], Jasmina Obhođaš[4]

[1] *Faculty of Science, Department of Geology, University of Zagreb, Horvatovac 95, HR-10000 Zagreb, Croatia*
[2] *Faculty of Science, Division of Biology, University of Zagreb, Rooseveltov trg 6, HR-10000 Zagreb, Croatia*
[3] *Geotechnical Faculty, University of Zagreb, Hallerova aleja 7, HR-42000 Varaždin, Croatia*
[4] *Department of Experimental Physics, Ruđer Bošković Institute, Bijenička c.54, HR-10000 Zagreb, Croatia*
** Corresponding author: E-mail: sabina.strmic@inet.hr*

ABSTRACT: The purpose of this study is to estimate the environmental impact of the siderite–polysulfide–barite–hematite Rude historical mining site as well as the influence of the urbanization on the quality of the draining streams. The Rude deposit is drained by the Gradna stream. According to obtained geochemical and bacteriological parameters the Gradna stream is divided into four segments: 1) The headwater (decreased pH, high Eh, low concentration of nitrogen and phosphorous species, metals and bacteria); 2) The segment between headwater and the historical mining site (uniform pH, gradual decrease in Eh and increase in NO_3^-, NH_4^+ and PO_4^{3-} concentrations); 3) The Rude historical mining site (slightly lower pH, high Eh, low NO_3^-, NH_4^+ and PO_4^{3-} concentrations, sudden increase in metals concentration in water and decrease in adsorbed metals) and 4) The segment between the mining site and the mouth is under strong influence of the urbanization (decreased Eh, increased NO_3^-, NH_4^+ and PO_4^{3-} concentrations, increased bacterial content) whereas influence of the historical mining site is diminished.

Keywords: Geochemistry, bacteriology, water, stream sediments, the Rude polymetallic ore deposit, Samoborska Gora Mts.

1. Introduction

The historical siderite–polysulfide–barite–hematite mining site Rude, Samoborska Gora Mts., is situated within the westernmost part of the Zagorje–Mid–Transdanubian zone of the Internal Dinarides (Palinkaš et al., 2010). The deposit is drained by the Rudarska Gradna creek. The creek originates approximately 1.8 km southwestern from the deposit. Generally, it runs southwest–northeastwards for about 16 km. In the upper part of the course the creek flows through rural area and it is fed by the several small streams. After its confluence with the Lipovečka Gradna creek it flows through the town of Samobor. The Gradna creek joins the Sava River in the vicinity of the Gradna village (Fig. 1).

Whereas polymetallic ore deposits represent geochemical anomalies of numerous potentially toxic metals, the purpose of the study was to determine the environmental impact of the historical mining site to geochemistry of stream water and stream sediments. Additionally, we examined correlations between geochemical parameters, bacteriological parameters and the degree of urbanization in the studied area.

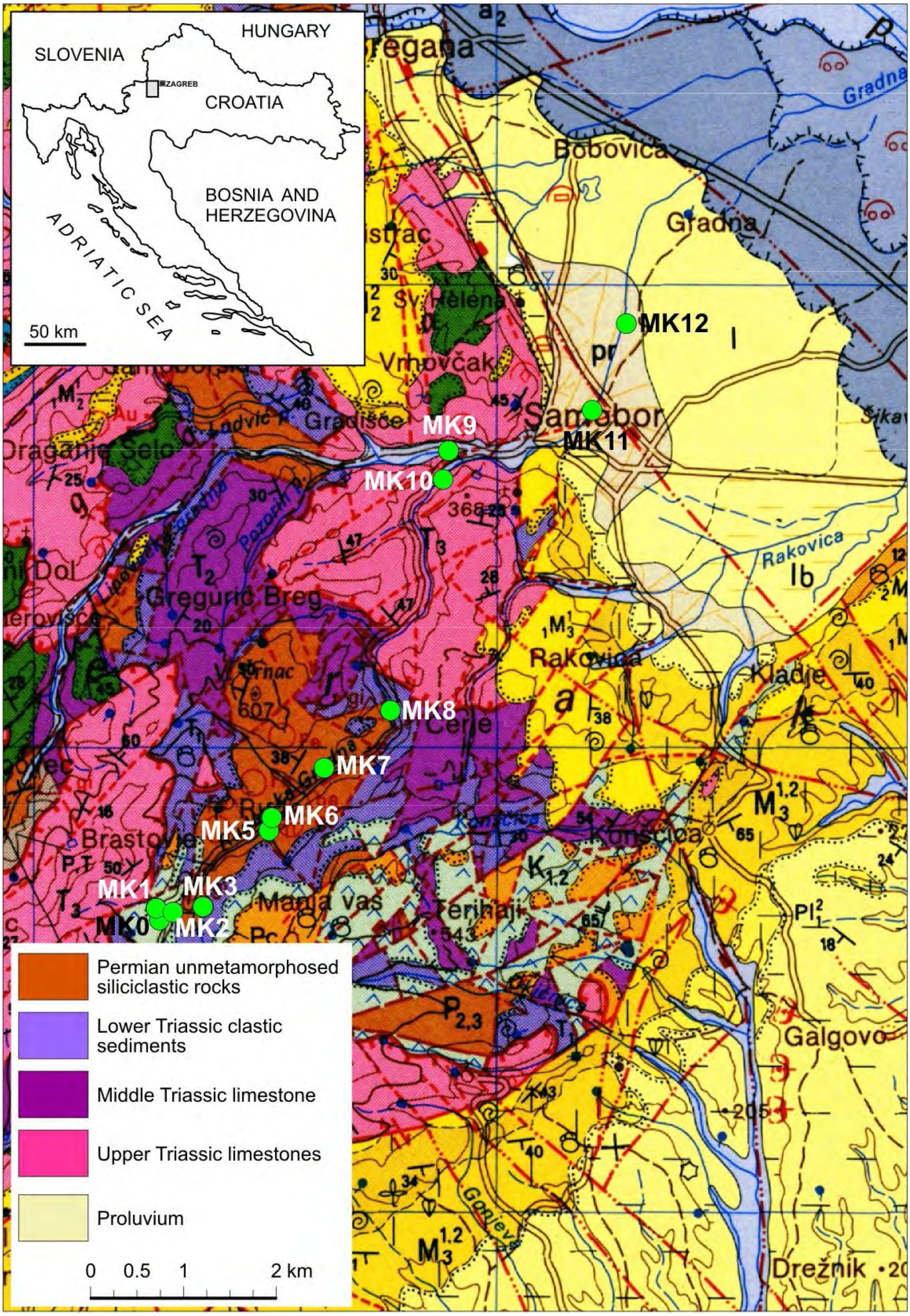


Fig. 1. Geographical and geological setting of the investigated area with marked sampling sites (MK0-MK12).

2. Geological setting and mineralization

The Samoborska Gora Mts. represents the westernmost part of the Zagorje Mid–Transdanubian zone (Pamić & Tomljenović, 1998; Tomljenović, 2002) or the Sava Composite unit (Haas et al., 2000). The mountain comprises Paleozoic, Mesozoic–Paleogene and Neogene formations.

The Autochthon of Samoborska Gora Mts. consists of: 1) Paleozoic unit, composed of Late Carboniferous dark gray schists, shales and sandstones. Shallowing of the sedimentary basin evolved into a dry-land phase, followed by deposition of fine to coarse–grained sandstones, interlayered with conglomerates, dolostones and evaporites (Herak, 1956). These deposits are uncomfortably overlain by an Early Triassic clastic–carbonate unit, followed by Middle and Late Triassic carbonate–marl sediments, with occasional appearances of cherts, and 2) Cretaceous mélange is predominantly composed of basalts and diabases within shales, graywackes, conglomerates, radiolarites and limestones of different Mesozoic ages, covered by Neogene sediments. The volcanics, often as basalt–spilite pillow lavas, might be products of a Triassic rifting stage. Allochthon is represented by Mesozoic carbonate platform lithotypes (Palinkaš et al., 2010, and references therein).

The Rude siderite–polysulfide–barite–hematite deposit comprises two principal ore types: 1) an epigenetic, hydrothermal vein-type and 2) a stratiform, SEDEX type. Epigenetic, epi-mesothermal, quartz–siderite veins with chalcopyrite, galena, sphalerite and barite, crosscut the Middle–Upper Permian clastic rocks. The epigenetic part of the deposit represents a feeder zone of the SEDEX, stratiform ore lenses formed in an evaporitic pond–lagoon by sedimentation of gypsum–anhydrite, hematite, siderite and barite. Laterally, epigenetic, epithermal barite–galena veins intersect Upper Permian coarse-grained sandstones. The deposit is covered by Lower Triassic variegated clastics (Šinkovec, 1971; Palinkaš et al., 2008). Mining activities in the area have lasting since the early 13th to the end of 19th century. According to Palinkaš et al. (2010) the Rude deposit is declared as a prototype of the Permian siderite–polysulfide–barite deposits produced during the early stage of the intracontinental rifting.

3. Sampling and methods

Stream water and sediments samples were collected during the sampling campaign in October 2010. The sampling sites are marked at Figure 1. Collection and sample handling were conducted in accordance to standard methodology for the analysis of the analyzed parameters (Feliks & Škunca-Milovanović, 1990; Rose et al., 1979).

Water temperature, pH, redox potential, electrical conductivity and dissolved oxygen (DO) measurements were conducted in situ on unfiltered water using a portable Hach Lange HQ40d Multimeasure Device.

Nitrate was electrochemically measured using a low-level calibrated nitrate-sensitive electrode (Hach Platinum Series combination electrode, model 51920) connected to a voltmeter (Hach SensIon 2). To avoid interference effects of bicarbonate ions the pH of samples was adjusted to 3 by the addition of acidic buffer (H_2SO_4).

Ammonia content was determined using Hach IntelliCAL™ ISENH3181 gas-sensing ammonia ion selective electrode (ISE) with a replaceable membrane module, refillable outer body, double junction reference and built-in temperature sensor. The measuring range is in an interval between 0.007 mg/L and 14,000 mg/L NH_3-N. The sample preparation procedure required the addition of alkaline buffer (LiOH) to ensure that the ammonia was essentially un-ionized prior to analysis.

Total phosphates were analyzed by the ascorbic acid method (APHA Standard Method 4500-P; APHA, AWWA, EFA, 1998). Absorbance was measured at 880 nm using a Hach DR4000 spectrophotometer.

Acidified sample solutions were used for heavy metal concentration measurements, using the flame atomic absorption method for Fe, Mn, Pb, Cu, and Zn and graphite furnace technique for Hg and Cd measurements (Perkin–Elmer AAnalyst 800).

Exchangeable metals were extracted from the stream sediments (m = 10 g) using 250 ml of 1 M NH_4OAc solution at pH =7.0. The sediment-solution slurry is shaken for 2 h, and the solution is separated from the solid by filtration. The addition of NH_4^+ in excess to the soil displaces the rapid exchangeable alkali and alkaline cations from the exchange sites of the soil particles. The concentrations of metals in the solution were measured with a Perkin-Elmer AAnalyst 800 Atomic Absorption Spectrometer.

Bulk stream sediment composition was estimated using energy dispersive X-ray fluorescence (EDXRF).

For cultivation of total and fecal coliform bacteria is used EC X-gluc agar (Biolife, Italy). Smear method was applied at 0.1 mL sample from the corresponding series of decimal dilutions. After incubation for 24 h at 44.5 ± 0.2 ° C for fecal coliforms and 48 h at 35 ± 0.5°C for total coliforms colonies of bacteria and E. coli colonies were counted. The number of bacteria is expressed as the number of colonies (CFU) per 1 L of sample and a percentage of E. coli in the sample is determined. For cultivation of saprophytic bacteria is used non-selective nutrient agar base (Biolife, Italy). Incubation lasts for 72 hours at a temperature of 22°C (Eaton et al., 2005).

4. Results

The **pH** value of water samples spans between 7.39 (sample MK0) and 8.69 (sample MK12) and according the Croatian water quality guidelines (OG 77/98) analyzed samples belong to the I. and II. category of water (Table 1).

Table 1. Bacteriological data obtain along the Gradna stream course.

Sample	**Total coliforms (CFU/L)**	***E.coli* (%) Total coliforms**	**Fecal coliforms (CFU/L)**	***E.coli* (%) F.coliforms**	**Saprophytes (CFU/L)**	**Water type**
MK0	$<5\times10^2$	0	$<2\times10^2$	0	$<10^3$	I
MK2	$1,51\times10^6$	0	$<2\times10^2$	0	$2,40\times10^4$	V
MK3	$1,2\times10^6$	0	$<2\times10^2$	0	$9,60\times10^4$	V
MK5	$3,2\times10^6$	0	$<2\times10^2$	0	$4,21\times10^5$	V
MK6	$7,74\times10^7$	0	$5,6\times10^5$	82	$4,61\times10^5$	V
MK7	$7,01\times10^7$	0,3	$6,2\times10^5$	35	$9,46\times10^5$	V
MK8	$1,97\times10^6$	5	$<2\times10^2$	0	$7,90\times10^4$	V
MK9	$3,65\times10^6$	0	$<2\times10^2$	0	$1,54\times10^5$	V
MK10	$9,01\times10^6$	0	$<2\times10^2$	0	$5,46\times10^5$	V
MK11	$4,13\times10^6$	0	$<2\times10^2$	0	$9,80\times10^4$	V

The concentration of **sulfate** (SO_4^{2-}), measured in the range between 3.1 mg/L (MK0) and 8.1 mg/L (MK7), is considerably lower than maximum allowable concentrations (MAC) regulated by Croatian regulative for drinking waters (OG 47/08). **Phosphates** (PO_4^{3-}), estimated in the interval from 0.01395 mg/L (MK0) to 0.1347 mg/L (MK11), classified all analyzed to the I category of water (OG 77/98). Concentration of **nitrate** (NO_3^-) was measured in the range between 4.86 and 66.81 mg/L. Samples MK0 and MK1 belong to the I category, while other samples are classified within the III category of water (OG 77/98). **Ammonia** (NH_4^+) spans between 0.0433 mg/L (MK 7) and 0.254 mg/L (MK8).

Figure 2 shows the distribution of iron in water as well as content of Fe adsorbed onto stream sediments.

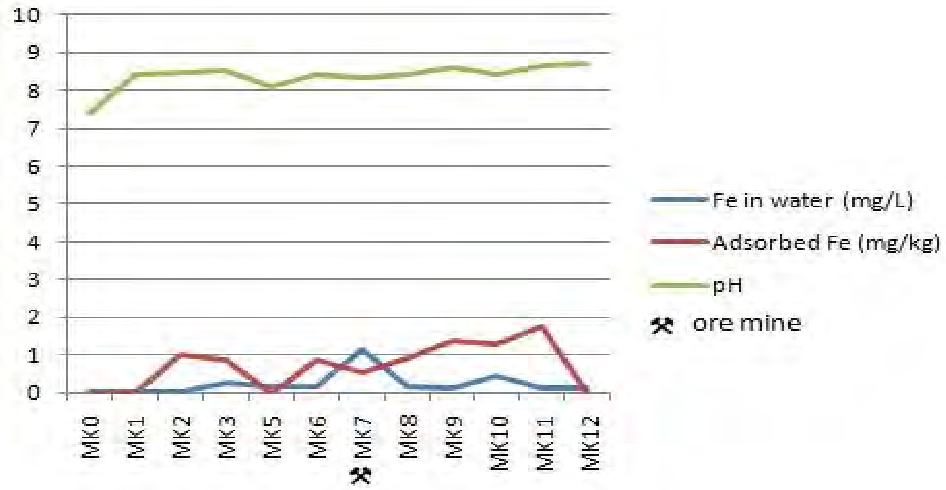


Fig. 2. Concentrations of dissolved and adsorbed iron estimated along the Gradna stream course. The measured pH values are presented as well.

The bulk potassium content for the sediments on siliciclastic terrain is comparatively higher than for the sediments on carbonate terrain, reflecting the lithological contribution of this element. The principal carriers of K are K-feldspars, biotite, micas and clay minerals. A expected, the highest Ca values are recorded for the stream sediments collected on carbonate terrains. The Fe concentration is generally lower than the average shale value. An exception is the sampling site MK7 near the Rude polymetallic ore deposit (Fig 3).

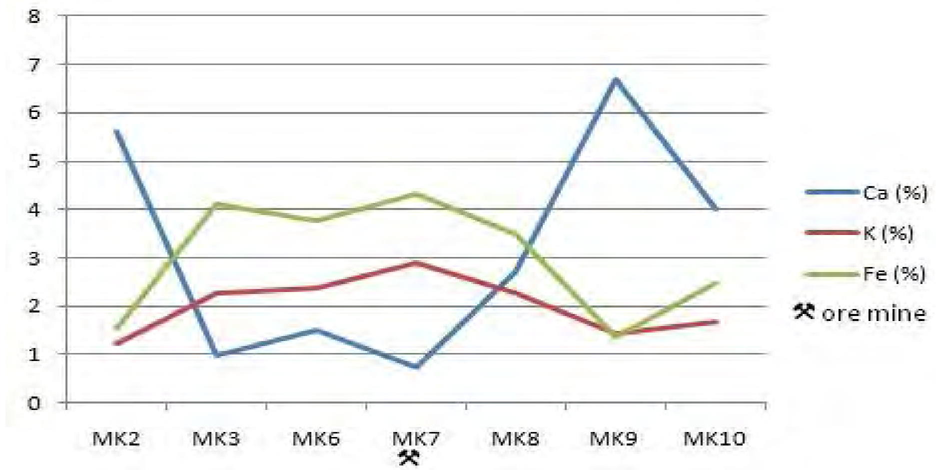


Fig. 3. Bulk concentrations of calcium, potassium and iron in stream sediment samples collected along the Gradna stream course.

5. Statistical treatment of data

To assess the influence of lithological substrate on water and stream sediment, and certain types of major lithological units are defined by percentage of the dominant rock types of the sampling points (Rose et al, 1970, Bonham-Carter et al 1987, Peh, 1992, Halamić et al, 2001). These units were used as lithological variables in the statistical analysis with markers LIT1-Triassic carbonates, LIT2-clastic Permian rocks, LIT3-proluvium.

Additionally, urbanization of area was introduced as a single variable.

Consequently for each sampling site 23 descriptors, consisting of 3 lithological, 19 geochemical and 1 urbanization variable, were observed and included in the statistical treatment.

6. Discussion

The primary ore mineralization usually is not stable under the surface conditions (low temperature and pressure, high activities of water, oxygen and CO_2). The mobility of metals depends mostly on pH and redox potential of solution as well as on possibility for the formation of complexes.

Although the Rudarska Gradna creek rises within Middle Triassic carbonate rocks, the headwater is characterized by slightly decreased pH value reflecting the strong influence of underlying siliciclastic sediments, mostly Cretaceous shales, sandstones and cherts (Fig. 1). Increased Eh value suggests the low organic matter content. The NO_3^-, NH_4^+ and PO_4^{3-} concentrations, as well as content of majority of analyzed metals are very low.

The segment between the headwater and the Rude mining site displays uniform pH value (pH≈8.5) despite to several small tributary streams with decreased. The progressive decrease in redox potential coincides with the increase in nitrate, ammonia and phosphate concentrations suggesting the common source of organic matter, nitrogen and phosphorous.

Water at the historical mining site is characterized by slight decrease in pH and increase in Eh value. Nitrates, ammonia and phosphates are significantly lower than in the main stream indicating the diminished influence of the anthropogenic pollution. Increased concentration of metals in water (Fe, Fig. 2) is expected due to the weathering of ore mineral assemblage. The decreased content of all exchangeable metals (Fe, Fig. 2) suggests the pH as a key parameter controlling the metal mobility. Under decreased pH, the competition between H^+ and the dissolved metals for ligands is more significant. It decreases the adsorption abilities of metals, and consequently increases their mobility.

The segment downstream from the Rude mining site display decrease in redox potential and increase in nitrogen and phosphorous species suggesting the enhanced influence of urbanization onto the water quality. The concentrations of metals in water, including Fe, gradually decrease downstream suggesting the diminishing influence of the ore deposit. Contrary, adsorbed iron content increase (Fig. 2) pointing to the stream sediment metal accumulation.

The positive correlation between measured pH values of stream water and the presence of Triassic carbonates (variable LIT1; r=0.53) is expected due to high buffering capacity of carbonate rocks. Electrical conductivity of water, the measure for the concentration of total dissolved solids, increases on the siliciclastic terrains (LIT2; r=0.54) and in the urban/rural areas as well (r=0.56). Mercury concentration in water correlates positively with proluviall sediments (LIT3; r_{Hg}=0.82). The increased Hg concentrations in the Sava river alluvium previously were attributed to the urbanization, industry and mining activities upstream (Namjesnik-Dejanović, 1994; Palinkaš et al., 1996; Halamić et al., 2003).

The populated areas highly correlate with the concentrations of nitrate (r=0.91), ammonia (r=0.86) and phosphate (r=0.64) indicating their common source, mostly from the domestic wastewaters in the areas without sewerage facilities. In the rural area agricultural activities, including the use of synthetic and organic fertilizers, might increase nitrate, ammonia and phosphate contents in the stream waters as well.

7. Conclusions

According to the principal geochemical features (pH, redox potential, conductivity, concentration of nitrogen and phosphorus species, heavy metal content in the stream water and in stream sediments) the Gradna creek might be divided into four segments: 1) The headwater (decreased pH, high Eh, low concentration of nitrogen and phosphorous species, metals and bacteria); 2) The segment between headwater and the historical mining site (uniform pH, gradual decrease in Eh and increase in NO_3^-, NH_4^+ and PO_4^{3-} concentrations); 3) The Rude historical mining site (slightly lower pH, high Eh, low NO_3^-, NH_4^+ and PO_4^{3-} concentrations, sudden increase in metals concentration in water and decrease in adsorbed metals) and 4) The segment between the mining site and the mouth is under strong influence of the urbanization (decreased Eh, increased NO_3^-, NH_4^+ and PO_4^{3-} concentrations, increased bacterial content) whereas influence of the historical mining site is diminished.

8. References

Bonham-Carter, G.F., Roger, P.J & Ellwood, D.J. (1987): Catchment basin analysis applied to surficial geochemical data, Cobequid Highlands, Nova Scotia.- J. Geochem. Explor., 29, 259-278.

Eaton, A. D., Clesceri, L. S., Rice, E. W., Greenberg, A. E. i Franson, M. A. (2005): Standard Methods for the Examination of Water and Wastewater, 21st Edition. American Public Health Association (APHA), American Water Works Association (AWWA) & Water Environment Federation (WEF).

Feliks & Škunca-Milovanović (1990): Voda za piće, Standardne metode za ispitivanje higijenske ispravnosti, Savezni zavod za zdravstvenu zaštitu, Beograd.

Halamić, J., Peh, Z., Bukovec, D., Miko, S., Galović, L. (2001). A Factor Model of the Relationship between Stream Sediment Geochemistry and Adjacent Drainage Basin Lithology, Medvednica Mt., Croatia. Geologia Croatica, 54/1, 37-51.

Halamić, J., Galović, L. & Šparica, M. (2003): Heavy Metals (As, Cd, Cu, Hg, Pb and Zn) Distribution in Topsoils Developed on Alluvial Sediments of the Drava and Sava Rivers in NW Croatia, Geologia Croatica, 56/2, 215-232.

Herak, M. (1956): Geologija Samoborskog gorja (Geologie des Samoborer Gebirges). Acta geol., 1, (Prir. istraž. 27), Jugosl. akad. znan. i umjetn., Zagreb, 49-73.

OG (1998): Uredba o klasifikaciji voda Republike Hrvatske. Narodne novine 77/98.

Haas, J., Mioč, P., Pamić, J., Tomljenović, B., Árkai, P., Bérczi-Makk, A., Koroknai, B., Kovács, S. & R.-Felgenhauer, E. (2000): Complex structural pattern of the Alpine-Dinaridic Pannonian triple junction. Int. J. Earth Sci. 89, 377-389.

Namjesnik, K. (1994): Distribucija teških metala u tlima grada Zagreba i njegove okolice. Magistarski rad, Rudarsko-geološko-naftni fakultet, Sveučilište u Zagrebu, 71 p., Zagreb.

Palinkaš, A. L., Namjesnik-Dejanović, K., Miko, S. F., Pirc, S. i Durn, G. (1996): Distribution of mercury, lead and cadmium in Zagreb city soils, Environmentač Xenobiotics, 355-374, Taylor & Francis Ltd., UK.

Palinkaš, L., Borojević Šoštarić, S. & Strmić Palinkaš, S. (2008): Metallogeny of the Northwestern and Central Dinarides and Southern Tisia. -Ore Geol. Rev., 34, 501-520.

Palikaš, A.L., Borojević Šoštarić, S., Strmić Palinkaš, S., Prochaska, W., Spangenberg, J., Cuna, S. & Šinkovec, B. (2010): Permian-polysulphide-siderite-barite-hematite deposit Rude i Samoborska Gora Mts., Zagorje-Mid-Transdanubian zone of the Internal Dinarides. Geologia Croatica, Zagreb, 63, 93-115.

Pamić, J. & Tomljenović, B. (1998): Basic geological data from the Croatian part of the Zagorje–Mid–Transdanubian Zone.– Acta Geol. Hungarica, 41, 389–400.

Peh, Z. (1992): Factor model of the geomorphological system of a part of Northwestern Croatia.- Geol. Croatica, 45, 163-172.

Rose, A.W., Dahlberg, E.C. i Keith, M.L. (1970): A multiple regression technique for adjusting backgroundvalues in stream sedisediment geochemistry.- Econ. Geol., 65,156-165.

Rose, A.W., Hawkes, H.E. i Webb, J.S. (1979): Geochemistry in mineral exploration.- 2nd ed., Academic Press, London, 657.

Šikić, K., Basch, O., Šimunić, A. (1978): Osnovna geološka karta SFRJ 1 : 100 000. List Zagreb. L 38-80. Institut za geološka istraživanja Zagreb, Savezni geološki zavod, Beograd 1972.

Šinkovec, B. (1971): Geologija ležišta željezne i bakrene rude u Ruda ma kraj Samobora [Geology of iron and copper ore from Rude near Samobor–in Croatian].– Geol. Vjesn., Zagreb, 24, 165–181.

Tomljenović, B. (2002): Strukturne karakteristike Medvednice i Samoborskog gorja [Structural characteristics of the Mts. Medvednica and the Samoborsko Gorje Mts. – in Croatian].– Unpubl. PhD thesis, University of Zagreb, 208 p.

THE USE OF DEPLETED URANIUM AMMUNITIONS DURING THE BALKAN CONFLICTS - POSSIBLE IMPACTS ON THE ENVIRONMENT

Goran Kniewald

Division for Marine and Environmental Research, Rudjer Boskovic Institute, POB 180, 10002 Zagreb, Croatia

Abstract: The NATO airstrikes on Kosovo (Yugoslavia) early in 1999 have caused considerable environmental damage to the broader region. Increased public concern regarding the dumping of unspent ordnance and the use of depleted uranium munitions during military operations, has resulted in several field campaigns by international organizations aimed at assessing possible risks to humans and the environment. Preliminary investigations have shown that some components of DU ordnance contain trace amounts of transuranics and fission products indicating the use of reprocessed uranium in the manufacture of these components. This study gives a summary of publicly available information on the environmental aspects of DU expenditure in Kosovo and the Adriatic region.

Keywords: Adriatic Sea, depleted uranium, diseases, ordnance, radioactivity, trace elements, uranium.

1. INTRODUCTION

The 11 weeks of North Atlantic Treaty Organization's (NATO) airstrikes in Kosovo (Yugoslavia) seem to have caused considerable environmental damage. A large number of industrial facilities were reportedly attacked and destroyed. As a consequence of this, significant amounts of hazardous chemicals have been released into surface waters, ground waters, air and soil, affecting the wider Balkans region. However, these transboundary pollution events have caused less public concern than subsequent admittance that the alliance had used depleted uranium (DU) ammunition both in Kosovo and during the earlier military operations in Bosnia and Herzegovina. Reports in public media have often echoed anger and dismay regarding the use of DU, suggesting that depleted uranium ordnance contributed to the "Balkan syndrome". Concerns were raised by governments which had peace-keeping troops deployed in the Kosovo region after the airstrikes, since a substantial number of soldiers developed health problems which were allegedly linked to DU. Similarities were established with the "Gulf War Syndrome" – an array of chronic illnesses that have apparently affected tens of thousands of US soldiers. In contrast, government contractors and the army itself have issued a series of reports and studies suggesting that depleted uranium represents no real threat to health and safety.

Moreover, serious concerns were raised over the possibility that ordnance, mainly aviation bombs, dumped in various parts of the Adriatic sea by aircraft returning to their bases in Italy, contained depleted uranium.

In this study, we have surveyed publicly available reports in an attempt to put these apparent controversies into perspective and summarize the environmental aspects of DU deployment during the NATO air campaign in Yugoslavia (Kosovo).

2. DEPLETED URANIUM (DU) AND ITS USE IN AMMUNITIONS

Uranium is a naturally occuring element, which has three principal isotopes: U-238 (99.2836 %), U-235 (0.7110 %) and U-234 (0.0054 %). Depleted uranium (DU) is a by-product (or waste) of the enrichment process used in the production of fuel rods for nuclear power plants and nuclear powered ships, as well as from the production of highly enriched uranium (U-235) for nuclear weapons. The radioactivity of natural uranium with its daughter products is around 50.000 Bq/g, while that of DU is ca. 40.000 Bq/g (i.e. about 20 % less). Chemically and toxicologically DU behaves in the same way as the metallic form of natural uranium. Fine particles of the metal ignite easily, producing oxides. Uranium causes kidney damage in experimental animals, and some studies indicate that long-term exposure may result in kidney damage to humans (Repacholi, 2001).

In addition to a number of peaceful applications (counterweights in aeroplanes, radiation shields in medical radiotherapy units and for transport of radioactive isotopes), DU is used for military purposes as tank armour, anti-tank munitions, missiles and projectiles due to its high density and melting point. DU weapons are regarded as conventional weapons. The International Committee on Radiation Protection (ICRP) does not list DU as a health hazard.

According to technical literature (referenced in Schmid and Wirz, 2000), a DU projectile upon impact – then being in the form of liquid or powder – starts burning, thereby increasing its destructive effects. The uranium metal vaporizes in the form of a uranium oxide aerosol, which presents an additional health risk to personell within the armored vehicle, as well as rescue teams. Possible health effects will depend on the route and magnitude of exposure (ingestion, inhalation, wound or contact) and on the characteristics of the DU aerosol such as particle size and solubility (Repacholi, 2001).

DU particles released as aerosols and dust may be carried by wind over considerable areas, and will eventually settle on the ground surface. It is dispersed in soil, particularly in areas of high rainfall. Cultivation of contaminated soil and use of contaminated water and food may pose health risks, but these are expected to be limited. Radiochemical toxicity would be expected to be the main health concern, rather than external radiation exposure.

3. USE OF DU ORDNANCE IN KOSOVO

During the spring 1999 airstrikes in Yugoslavia (Kosovo), NATO fired some 31.000 depleted uranium shells (NATO website on depleted uranium, Figure 1). The alliance has recently released detailed grid locations where their aircraft engaged targets in Yugoslavia and earlier in Bosnia 1993-1995 (Data concerning the locations of depleted uranium ordnance expended during Operation Allied Force and Deny Flight-Deliberate Force /grid coordinates/). Reportedly all DU ordnance was 30mm aircraft-cannon munitions fired from A-10 "Warthog" anti-tank combat aircraft and AH-64 Apache helicopters used in air-to-ground missions. The ammunition was of the *PGU-14/B API Armor Piercing Incendiary* type. It consists of a lightweight body with a subcalibre high-density DU penetrator weighing 0.3 kg. In addition to its penetrating capability, the DU is a natural pyrophoric material which enhances incendiary effects.

A simple calculation yields the result that at least 10 tons of DU have been deployed. Some of this ammunition still litters various parts of the area, causing concerns about environmental contamination and human health risks.

Following an apparent policy of information transparency and full disclosure, much data including maps of targeted areas have been made publicly available and accessible on the NATO websites.

Fig.1. Sites in Kosovo identified as being targeted by ammunition containing DU

According to available reports (NATO website on depleted uranium), aviation bombs (both smart weapon systems and "dumb" bombs) used in operations against unarmored ground targets (military installations, industries and other structures) contained no DU components. Undeployed ordnance was discarded in waters of the Adriatic sea by aircraft returning to their bases (mainly in Italy, and carrier vessels stationed in the Adriatic).

4. RESULTS OF ANALYSES ON SAMPLES FROM DEPLETED URANIUM SITES IN KOSOVO

As a consequence of increased public concern and government inquiries into the NATO alliances use of DU ordnance in Kosovo, several investigation teams and expert groups (UNEP, WHO) were dispatched to Kosovo with the task of sample collection from targeted areas, in order to provide independent analyses and provide guidelines for possible remediation projects.

UNEP's Depleted Uranium Assessment Group, during its field assessment mission in November 2000, visited 11 of the 112 sites that were identified as being targeted by DU ordnance. Altogether, 340 samples were collected for analysis in 5 european laboratories. The samples include 247 soil samples, 30 vegetation samples, 10 smear tests, 8 parts of munition parts (sabots and penetrators). The final report is scheduled for publication in March 2001, but preliminary reports state that in addition to the "expected" uranium isotopes, parts of DU ordnance contained U-236 (0.0028 % of the total uranium content) and traces of other fission products, implying that these components were made from reprocessed uranium (UNEP Balkans press release). Following this disclosure, a report by the Department of the Army of the United States of America, dated January 2000, was made public (Report by the US Department of Army, 2000). The report states that DU components used by the US armed forces may contain trace amounts of transuranics (TRU) and Tc-99. The TRU may contain Am-241, Np-237, Pu-238, Pu-239 and Pu-240. However, the TRU contamination of DU components contributed an additional 0.8 % to the radiation dose from the DU itself, considering this a very low radiological hazard associated with the primary DU material.

5. CONCLUSIONS

Clearly, ammunition containing DU components leave behind a long-lasting contamination on the battlefields, which is not compatible with civil radiation protection norms. This argument holds independently whether or not there is an objective immediate or long-term danger to man and the environment.

Transuranium elements and other fission products possibly contaminating DU ordnance cause additional public concerns over risks to the health of humans and the environment, especially in the case of countries producing DU ordnance where manufacturing technologies may not necessarily meet US standards in the purification of uranium coming from spent nuclear fuel.

Ordnance dumped in the Adriatic Sea reportedly contained no DU munitions. An understanding of the biogeochemical uranium cycle in the marine environment provides no apparent reason for concerns regarding radiological hazards of DU. Uranium is present in seawater at an average concentration of 3.3 ug/L, mainly in the form of the highly soluble uranyl-tricarbonate complex. Uranium concentration factors in sediments and marine biota are small, so even if moderate quantities of DU ordnance were dumped in the sea, this would not be the cause of hazardous uranium levels in the marine environment. Nevertheless, we believe that these weapons should be retrieved and disposed of, especially in cases where ordnance was dumped in shallow parts of the Adriatic Sea, since they may pose a distinct and immediate threat to the fishing industry in the region.

Complete reports with full disclosure of the relevant facts regarding DU deployment in the Balkans and in the adriatic region will be welcomed by the scientific community and civilian population living in affected regions.

REFERENCES

Fetter, S. and F. von Hippel (1999). After the dust settles. *Bull.of the Atomic Scientist,* **55/6**, 42-45.

Repacholi, M.H. (2001). Background material on depleted uranium. *WHO Fact Sheet No. 257,* Geneva, Switzerland.

Schmid, E. and Ch. Wirz (2000). Depleted uranium. Background information on a current topic. AC – Laboratorium Spiez report, Spiez, Switzerland.

Analysis of Transuranics and Other Contaminants in Depleted Uranium Armor. *Report by the Department of the US Army – AMSAM-TMD-SB, January 2000.*

Data concerning the locations of depleted uranium ordnance expended during Operation Allied Force (grid co-ordinates). *http://www.nato.int/du/docu/d010124a.htm*

Data concerning the locations of depleted uranium ordnance expended during Operations Deny Flight–Deliberate Force, 1993-95 in Bosnia (grid co-ordinates). *http://www.nato.int/du/docu/d010124b.htm*

NATO website on Depleted Uranium (and references and links contained therein). *http://www.nato.int/du/home-new.htm*

UNEP confirms Uranium-236 found in DU penetrators. UNEP Balkans Press Release, 16 January 2001. *http://balkans.unep.ch/press/press010116.html*

DISTRIBUTION AND BEHAVIOR OF SELECTED ELEMENTS IN THE VELIKI POTOK/ČRNOMEREC CREEK, MEDVEDNICA MTS., CROATIA

Maša Martinić[1], Sabina Strmić Palinkaš[1,*], Ladislav Palinkaš[1],
Štefica Kampić[1], Dragana Dogančić[2]

[1] *Faculty of Science, Geological department, University of Zagreb, Horvatovac 95, HR-10000 Zagreb, Croatia*
[2] *Geotechnical Faculty, University of Zagreb, Hallerova aleja 7, HR-42000 Varaždin, Croatia*
**Corresponding author: E-mail: sabina.strmic@inet.hr*

ABSTRACT: The Veliki Potok/Črnomerec creek, Medvednica Mts., originates near the historical Pb-Zn-Ag mining site. The upper course of the creek flows through the Nature Park Medvednica presenting uninhabited and preserved nature area. The lower course flows through the city of Zagreb presenting urbanized area. Chemical characteristics of the stream water and sediment from the creek were investigated to examine the effects of historical mining activity and urbanization on the quality of water. Temperature, pH, redox potential, dissolved oxygen and conductivity of stream water were measured *in situ*. Concentrations of nitrates, ammonia, sulphates, phosphates and chlorides were determined in a laboratory. Concentration of heavy metals in stream water, as well as exchangeable metals content in stream sediments were estimated by atomic absorption spectrometry. According to obtained geochemical parameters, the Veliki Potok creek was divided into two principal segments. The upper course is characterized by moderate pH, high redox potential, low nitrate, ammonia, phosphate and sulfate concentration, as well as with low content of all analyzed metals with exception of manganese. The lower course shows high pH value, low redox potential, increased conductivity, increased content of nitrogen and phosphorous species and increased concentration of mercury and copper. The stream sediments from the lower course are characterized by high content of exchangeable metals, especially lead, zinc and copper.

Keywords: Geochemistry, water, stream sediments, the Sv. Jakob MVT deposit, Medvednica Mts.

1. Introduction

The Veliki Potok creek originates on the southern slopes of Medvednica Mts., Croatia, at an altitude of about 830 m. Source of the creek is situated near the historical Pb-Zn-Ag mining site (Fig. 1). The Sv. Jakob Pb-Zn-Ag deposit occurs in the Middle Triassic dolostone and displays features characteristic for the Mississippi Valley type of mineralization (Palinkaš et al., 2008). The most abundant ore mineral is galena containing up to 500 mg/kg of silver. Sphalerite and pyrite are present as well. The principal gangue minerals are calcite and quartz (Šinkovec et al., 1988; Durn et al., 1999; Palinkaš et al., 2008).

The upper course of the streams flows through the Nature Park Medvednica presenting uninhabited area and also a preserved nature area. The stream then enters into the city of Zagreb presenting urbanized area. The objective of this study was to determine the environmental impact of the historical mining site and urbanized area of the city of Zagreb to geochemistry of stream water and sediments.

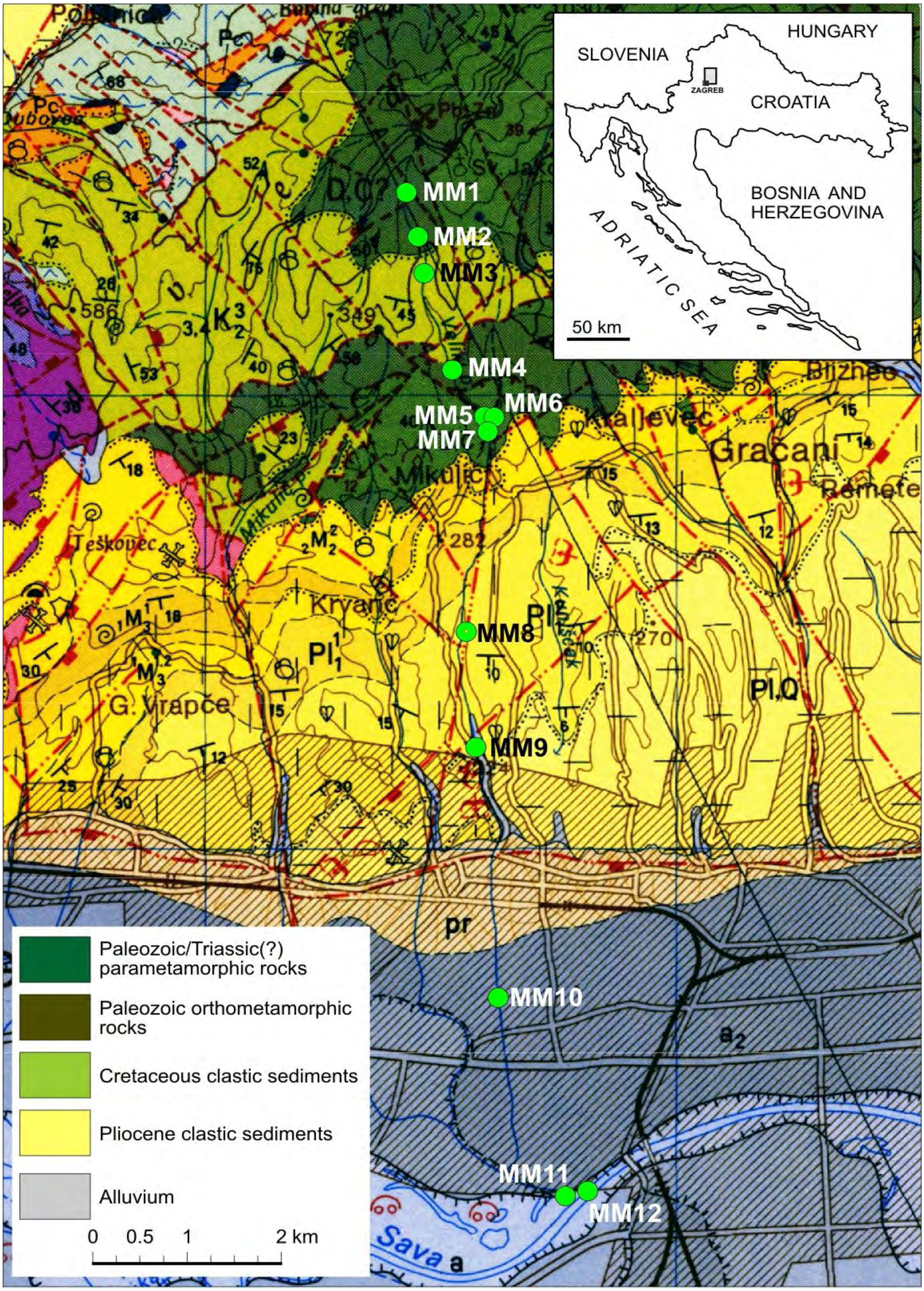


Fig. 1. Geographical and geological setting of the investigated area with marked sampling sites (MM1-MM12)

2. Geological setting

Tectonostratigraphic units of the Medvednica Mts. are grouped into four main units: 1) Tectonized ophiolite mélange, including all lithological members, from sediments, to mafic and ultramafic igneous components; 2) Paleozoic–Triassic magmatic–sedimentary complex overprinted by Early Cretaceous metamorphism; 3) Late Cretaceous–Paleocene flysch, and Allochthon: 4) Triassic and younger sequences belonging mainly to carbonate platform facies (Šikić et al., 1978; 1979; Šikić, 1995; Palinkaš et al., 2010).

3. Mineralization

The Sv. Jakob Pb–Zn-Ag deposit is hosted by non-metamorphosed Middle Triassic dolostone (Palinkaš et al., 2008). The ore occurs in forms of veinlets and lenses. The principal ore mineral is coarse grained galena containing up to 500 mg/kg of silver. The vein-type mineralization, beside galena, comprises minor sphalerite, pyrite, quartz and calcite (Šinkovec et al., 1988). The ore has been actively mined during the 17th century. According to the epigenetic character of the ore mineralization, simple ore paragenesis without copper minerals and the fluid inclusions and sulfur isotope data the deposit is classified as the Mississippi Valley type of Pb–Zn deposits (Šinkovec et al., 1988; Durn et al., 1999; Borojević Šoštarić, 2004; Palinkaš et al., 2008).

The deposit is situated at an altitude of 830 m above sea level, approximately 300 m north from the Veliki Potok creek headwater. The Veliki Potok creek runs north–southwards for about 12 km. In the upper part of the course the Veliki Potok is fed by the Mali Potok creek and by numerous small streams. The central and lower part of the creek flows through the urban area of Zagreb. In the lowermost part of the course, about 500 m upstream from its mouth into the Sava River, the Veliki Potok confluents with the Vrapčak creek. The Veliki Potok originates in Paleozoic orthometamorphic complex, referred to the Devonian-Carboniferous age (Fig. 1). Continuing downstream, the creek is entrenched in the Cretaceous sedimentary rocks predominantly represented by fine-grained clastics. The Paleozoic parametamorphic complex comprises greywackes, siltstones, limestones, dolostones, muscovite-chlorite and muscovite-quartz schists (Šikić et al., 1978; 1979). According to several authors (e.g. Đurđanović, 1973; Belak et al., 1995) some protoliths from the parametamorphic complex are of Triassic age. Further, the creek flows through the Neogene sediments represented mostly by sandstones, marls and limestones. The lowermost part of current dissects the Sava river alluvial sediments (Šikić et al., 1978; 1979).

3. Samples and methods

Stream water and sediments samples were collected during the sampling campaign in October 2010. The sampling sites are listed in Table 1 and marked at Figure 1.

Collection and sample handling were conducted in accordance to standard methodology for the analysis of the analyzed parameters (Feliks & Škunca-Milovanović, 1990; Rose et al., 1979).

Water temperature, pH, redox potential, electrical conductivity and dissolved oxygen (DO) measurements were conducted in situ on unfiltered water using a portable Hach Lange HQ40d Multimeasure Device.

Nitrate was electrochemically measured using a low-level calibrated nitrate-sensitive electrode (Hach Platinum Series combination electrode, model 51920) connected to a volt meter (Hach SensIon 2). To avoid interference effects of bicarbonate ions the pH of samples was adjusted to 3 by the addition of acidic buffer (H_2SO_4).

Table 1. The list of sampling sites with the corresponding properties

Sample	Gauss-Krüger coordinates		Lithology	Sample site description
	x	y		
MM-1	5572129	5082230	Paleozoic/Triassic(?) parametamorphic rocks	The Veliki Potok creek
MM-2	5572251	5081745	Paleozoic/Triassic(?) parametamorphic rocks	The Veliki Potok creek
MM-3	5572316	5081344	Cretaceous clastic sediments	The Veliki Potok creek
MM-4	5572617	5080280	Paleozoic/Triassic(?) parametamorphic rocks	The Veliki Potok creek
MM-5	5572958	5079768	Paleozoic orthometamorphic rocks	The Veliki Potok creek
MM-6	5573059	5079758	Paleozoic orthometamorphic rocks	The Mali Potok creek
MM-7	5572994	5079604	Paleozoic orthometamorphic rocks	The Veliki Potok creek
MM-8	5572763	5077404	Pliocene clastic sediments	The Veliki Potok creek, urban area
MM-9	5572867	5076130	Pliocene clastic sediments	The Veliki Potok creek, urban area
MM-10	5573103	5073379	Alluvium	The Veliki Potok creek, urban area
MM-11	5573816	5071199	Alluvium	The Veliki Potok creek, urban area
MM-12	5574057	5071255	Alluvium	The Sava River

Ammonia content was determined using Hach IntelliCAL™ ISENH3181 gas-sensing ammonia ion selective electrode (ISE) with a replaceable membrane module, refillable outer body, double junction reference and built-in temperature sensor. The measuring range is in an interval between 0.007 mg/L and 14,000 mg/L NH_3-N. The sample preparation procedure required the addition of alkaline buffer (LiOH) to ensure that the ammonia was essentially un-ionized prior to analysis.

Total phosphates were analyzed by the ascorbic acid method (APHA Standard Method 4500-P; APHA, AWWA, EFA, 1998). Absorbance was measured at 880 nm using a Hach DR4000 spectrophotometer.

Acidified sample solutions were used for heavy metal concentration measurements, using the flame atomic absorption method for Fe, Mn, Pb, Cu, and Zn and graphite furnace technique for Hg and Cd measurements (Perkin–Elmer AAnalyst 800).

Exchangeable metals were extracted from the stream sediments (m = 10 g) using 250 ml of 1 M NH_4OAc solution at pH =7.00. The sediment-solution slurry is shaken for 2 h, and the solution is separated from the solid by filtration. The addition of NH_4^+ in excess to the soil displaces the rapid exchangeable alkali and alkaline cations from the exchange sites of the soil particles. The concentrations of metals in the solution were measured with a Perkin-Elmer AAnalyst 800 Atomic Absorption Spectrometer.

4. Statistical treatment of data

Statistical treatment of data was done using Statistica 10 program package (StatSoft, Inc. (2011). The effects of lithology, conveyed through the lithological variables, were defined as a percentage of the drainage basin area which is occupied by a dominant rock type (Bonham-Carter et al., 1987; Peh, 1992). Four lithological variables were defined in investigated area: 1) Variable 1 is represented by Paleozoic/Triassic parametamorphic complex (samples MM1, MM2 and MM 4); 2) Variable 2 comprises Paleozoic orthometamorphic rocks (samples MM5, MM6 and MM7); 3) Variable 3 comprises Cretaceous and Pliocene clastic sediments (samples MM3, MM4, MM8 and MM9); 4) Variable 4 is represented by alluvium (samples MM10, MM11 and MM12). Additionally, urbanization of area was introduced as a single variable. Consequently for each sampling site 24 descriptors, consisting of 4 lithological, 19 geochemical and 1 urbanization variable, were observed and included in the statistical treatment.

5. Results

According to the Croatian water quality guidelines (OG 77/98), analyzed stream water samples are classified within Class I concerning pH (Fig. 2a) and dissolved oxygen (Fig. 2b) and Classes I and II concerning conductivity (Fig. 2c). The Eh value gradually decreases downstream (Fig. 2d).

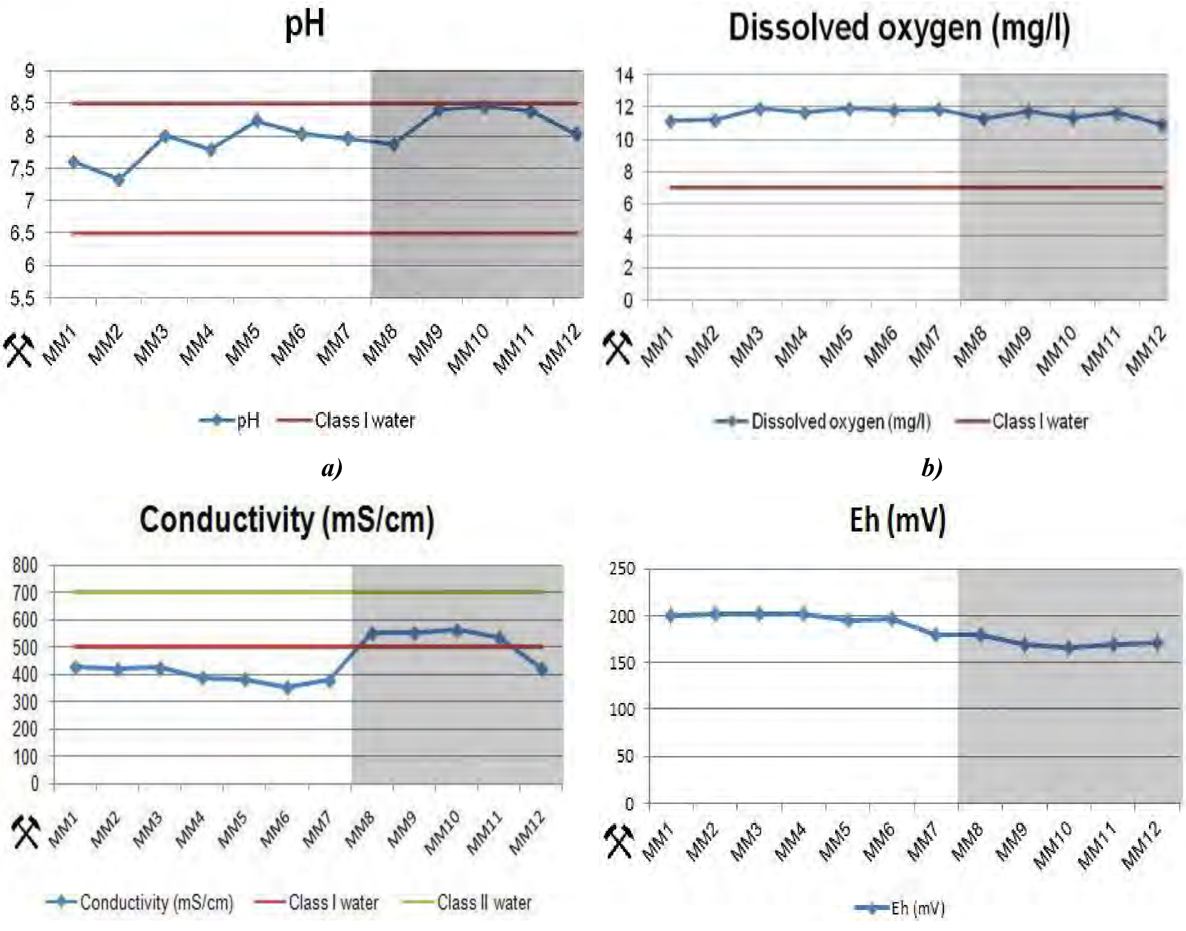
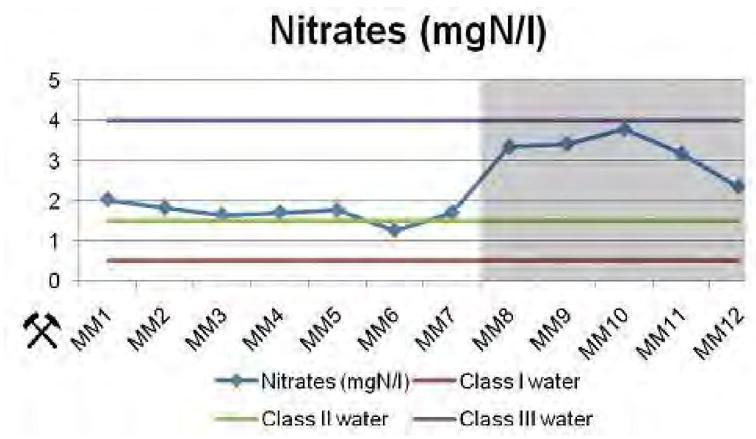
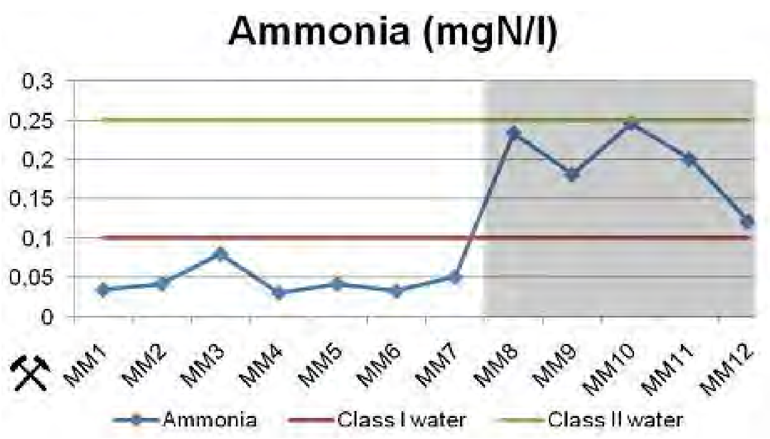


Fig. ***2a)*** Line plot of pH value mesured *in situ;* ***2b)*** Line plot of concentrations of dissolved oxygen measured *in situ;* ***2c)*** Line plot of conductivity measured *in situ;* ***2d)*** Line plot of redox potential measured *in situ*

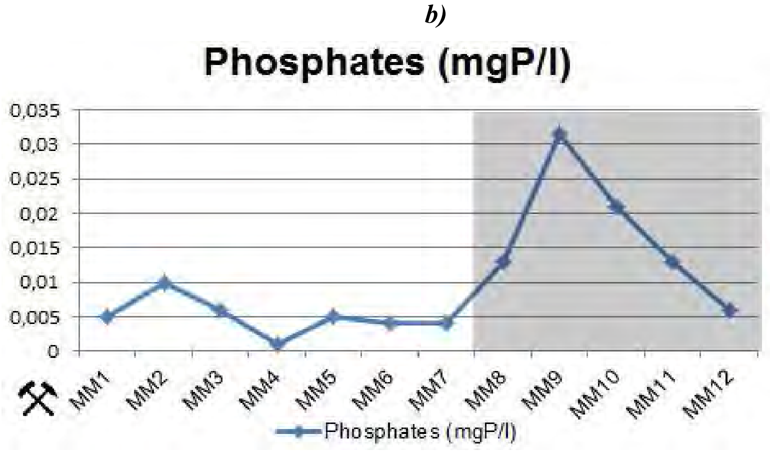
According to nitrate (Fig. 3a) and ammonia concentrations (Fig. 3b) the water samples belong to Classes II and III, respectively. The results for total phosphorus classify all samples within Class I (3c). Measured concentrations of sulfates and chlorides were considerably lower than maximum allowable concentrations (MAC) regulated by Croatian regulative for drinking waters (OG 47/08).



a)



b)

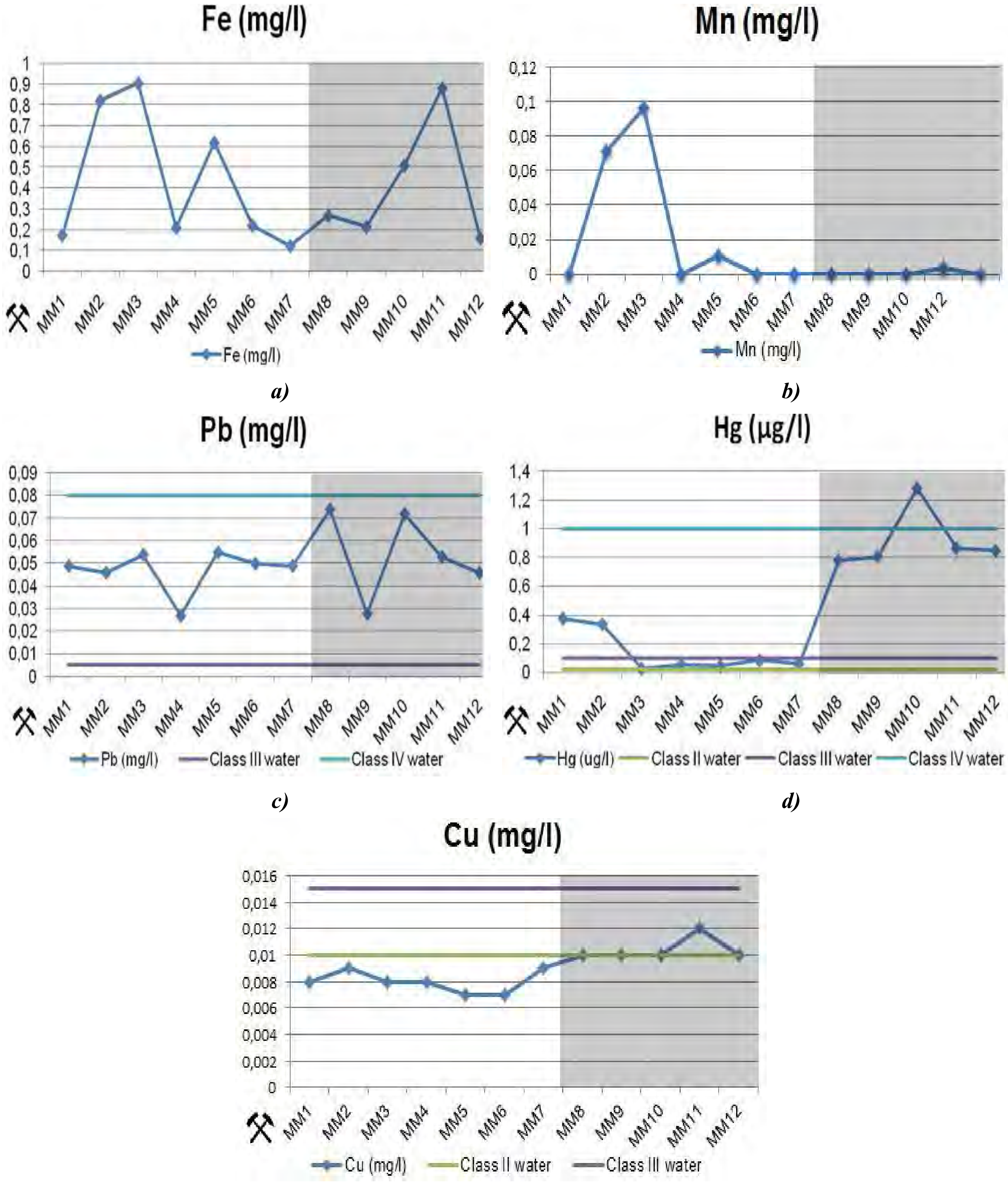


c)

Fig. ***3a)*** Line plot of nitrate concentrations in water samples; ***3b)*** Line plot of ammonia concentrations in water samples; ***3c)*** Line plot of phosphate concentrations in water samples

Iron (Fig. 4a) and manganese concentrations (Fig. 4b) in water samples are below the MAC for drinking waters. Elevated lead content classifies analyzed samples within Classes

IV and V. Increased concentration of lead in urban areas suggests its anthropogenic origin (Fig 4c). According to mercury concentrations of the water samples mostly belong to Class IV (Fig. 4d). Copper level varies from Class I to Class III (Fig. 4e). Low concentrations of zinc and cadmium are within the ranges proposed for Class I.



a) *b)* *c)* *d)* *e)*

Fig. ***4a)*** Line plot of iron concentrations in water samples; ***4b)*** Line plot of manganese concentrations in water samples; ***4c)*** Line plot of lead concentrations in water samples; ***4d)*** Line plot of mercury concentrations in water samples; ***4e)*** Line plot of copper concentrations in water samples

A summary of NH_4OAc extracted contents of Fe, Mn, Pb, Zn, Cu, Hg and Cd in stream sediments is given in Table 2.

Table 2. A summary of NH_4OAc extracted contents of Fe, Mn, Pb, Zn, Cu, Hg and Cd in stream sediments

Sample	Fe	Mn	Pb	Zn	Cu	Hg	Cd
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(μg/kg)	(μg/kg)
MM1	1.075	73.150	0.775	<*d.l*	0.475	<*d.l.*	11.125
MM2	0.875	83.475	0.750	0.525	0.400	<*d.l.*	38.575
MM3	1.000	101.250	<*d.l.*	<*d.l.*	0.275	900	25.325
MM4	1.400	49.575	<*d.l.*	<*d.l.*	0.475	<*d.l.*	15.450
MM5	2.075	85.125	0.525	<*d.l.*	0.650	<*d.l.*	10.950
MM6	1.775	62.350	0.700	<*d.l.*	0.600	1650	28.575
MM7	1.450	53.575	0.625	<*d.l.*	0.425	<*d.l.*	26.775
MM8	1.875	40.425	1.525	0.925	0.625	<*d.l.*	22.925
MM9	1.775	69.400	1.550	2.125	0.700	<*d.l.*	57.475
MM10	1.975	62.300	1.700	3.425	0.950	<*d.l.*	6.625
MM12	1.900	14.825	1.700	1.000	0.500	<*d.l.*	40.225

<*d.l.* – below detection limit

6. Discussion

According to the geochemical features the Veliki Potok creek is divided into 2 segments: 1) the upper course flows through an uninhabited area and 2) the lower course flows through the urban area. The upper segment of the creek is characterized by moderate pH and high redox potential. Increased Eh value suggests the low organic matter content. The NO_3^-, NH_4^+ and PO_4^{3-} concentrations, as well as content of all analyzed metals, with exception of manganese, are very low (Fig. 4b). Increased Mn concentration might be attributed to the remobilization of manganese from the Middle Triassic sediments. The low heavy metals content in the upper course, as well as low sulfate concentration, indicate that the Sv. Jakob Pb-Zn-Ag deposit does not represent the potential pollution source for the draining streams.

The lower part of the creek is characterized by increased pH value especially in the segment of the course which runs over alluvial sediment (MM10-MM12). Increased conductivity of stream water within populated area generally points to higher content of total dissolved solids. The progressive decrease in redox potential coincides with the increase in nitrate, ammonia and phosphate concentrations suggesting the common source of organic matter, nitrogen and phosphorous, mostly from the domestic wastewaters in the urban areas without sewerage facilities. The agricultural activity in the suburbs, including the use of synthetic and organic fertilizers, might increase nitrate, ammonia and phosphate contents in the stream waters as well. Furthermore, the urban area statistically correlates with the concentration of copper ($r=0.81$) and mercury in the stream water ($r=0.67$) and with the content of exchangeable lead ($r=0.85$), zinc ($r=0.86$) and copper ($r=0.71$) from the stream sediments.

For the appropriate interpretation of the heavy metals origin, it is important to keep in mind that the populated areas are mostly located on the alluvial deposits (LIT4; $r=0.48$; Fig. 1). The increased Hg concentrations in the Sava river alluvium were attributed to the mining and smelting activities upstream (Namjesnik-Dejanović, 1994; Palinkaš et al., 1996; Halamić et al., 2003).

7. Conclusion

The principal geochemical features (pH, redox potential, conductivity, concentration of nitrogen and phosphorus species, heavy metal content in the stream water and in stream sediments) are significantly different for the upper and lower course of the Veliki Potok/Črnomerec creek.

The creek originates near the historical Pb-Zn-Ag mining site and its upper course flows through an uninhabited area mostly over the Paleozoic orthometamorphic and parametamorphic rocks. This segment of the creek is characterized with moderate pH, high redox potential, low nitrate, ammonia, phosphate and sulfate concentration, as well as with low content of all analyzed metals with exception of manganese.

The lower segment of the creek flows through the urban area over Pliocene clastic sediments and alluvial deposit. This segment displays high pH value, low redox potential, increased conductivity, increased content of nitrogen and phosphorous species and increased concentration of mercury and copper. The stream sediments from the lower course are characterized by high content of exchangeable metals, especially lead, zinc and copper.

8. Reference

Belak, M., Pamić, J., Kolar-Jurkovšek, T., Peckay, Z. & Karan, D. (1995): Alpinski regionalnometamorfni kompleks Medvednice (sjeverozapadna Hrvatska) [Alpine regional metamorphic complex of the Medvednica Mt. - NW Croatia].- 1. hrvatski geol. kongres, Zbornik radova, 1, 67-70, Zagreb.

Bonham-Carter, G.F., Rogers, P.J., Ellwood, D.J. (1987): Catchment basin analysis applied to surficial geochemical data, Cobequid Highlands, Nova Scotia. Journal of Geochemical Exploration, 29, 1-3, 259-278.

Borojević-Šoštarić, S. (2004): Geneza sideritno-baritno-polisulfidnih ležišta u paleozoiku Unutrašnjih Dinarida [Genesis of siderite–barite–polysulphide ore deposits within Palaeozoic of Internal Dinarides – in Croatian].–Unpublished Masters thesis, University of Zagreb, 120 p.

Đurđanović, Ž. (1973): O paleozoiku i trijasu Medvednice (Zagrebačke gore) i područja Dvora na Uni na temelju konodonta [About the Paleozoic and the Triassic of Medvednica Mt. and the area near Dvor na Uni on the basis of conodonts].- Geol. Vjesn., Zagreb, 25, 29-49.

Durn, G., Miko, S., Čović, M., Barudžija, U., Tadej, N., Namjesnik-Dejanović; K. & Palinkaš, L. (1999): Distribution and behaviour of selected elements in soil developed over a historical Pb–Ag mining site at Sv. Jakob, Croatia. J. Geochem. Explor., 67, 361–376.

Feliks, R., & Škunca - Milovanović, S. (1990): Voda za piće, standardne metode za ispitivanje higijenske ispravnosti. Savezni zavod za zdravstvenu zaštitu, NIP "Privredni pregled", 844.

Halamić, J., Galović, L., Šparica, M. (2003): Heavy Metal (As, Cd, Cu, Hg, Pb and Zn) Distribution in Topsoil Developed on Alluvial Sediments of the Drava and Sava Rivers in NW Croatia, Geologia Croatica, 56/2, 215-232.

Halamić, J., Peh, Z., Bukovec, D., Miko, S., Galović, L. (2001): A Factor Model of the Relationship between Stream Sediment Geochemistry and Adjacent Drainage Basin Lithology, Medvednica Mt., Croatia. Geologia Croatica, 54/1, 37-51.

Namjesnik, K., Palinkaš, L.A., Miko, S., Durn, G., Polić, D., Kvrgnjaš L. (1992): Lead, Zinc and Mercury in Soil along Road Sides and of Some rural and Urban Parts of Zagreb, Croatia. Rudarsko-metalurški zbronik, 39, 1-2, 93-112, Ljubljana.

OG 47/08: Regulation on health safety of drinking water. Narodne novine (2008): Pravilnik o zdravstvenoj ispravnosti vode za piće. No 47, 16 p.

OG 77/98: Water classification act. Narodne novine (2008): Uredba o klasifikaciji voda. No 77, 16 p.

Palinkaš, L., Borojević-Šoštarić, S. & Strmić Palinkaš, S. (2008): Metallogeny of the Northwestern and Central Dinarides and Southern Tisia. -Ore Geol. Rev., 34, 501-520.

Palinkaš, L., Borojević-Šoštarić, S., Strmić Palinkaš, S., Prochaska, W., Spanderberg, J., Cuna, S. & Šinkovec, B. (2010): Permian–polysulphide-siderite–barite–haematite deposit Rude in Samoborska Gora Mts., Zagorje–Mid–Transdanubian zone of the Internal Dinarides. –Geol. Croat., 63, 93–115.

Rose, A. W; Hawkes, H. E. & Webb, J. (1979): Geochemistry in mineral exploration (2nd edition). Academic Press (London and New York), 657 p.

Šikić, K. (1995): Geološki vodič Medvednice.– Zagreb: Inst. geol.istraž., Zagreb, 199 p.

Šikić, K., Basch, O. & Šimunić, A. (1978): Osnovna geološka karta SFRJ 1:100 000. List Zagreb. L33–80 [Basic geological map of SFRY 1:100000, Zagreb sheet – in Croatian].– Inst. geol. istraž., Zagreb (1972), Sav. geol. zavod, Beograd.

Šikić, K., Basch, O. & Šimunić, A. (1979): Tumač osnovne geološke karte 1:100000, list Zagreb.– Sav. geol. zavod, Beograd, 81 p.

Šinkovec, B., Palinkaš, L. & Durn, G. (1988): Ore occurrences on Mt. Medvednica (in Croatian with English summary). -Geol. Vjesn., Zagreb, 41, 395–405.

WEB REFERENCES:

1. http://www.statsoft.com/support/free-statistica-10-trial/, 1.8.2011

Rb, Sr, K, and Pb IN THE SOILS OF TIKVES AREA

Blažo Boev[1], Vladimir Bermanec[2], Šorša Ajka[3]

[1]*Faculty of Natural and Technical Sciences, "Goce Delcev" University, Stip, Macedonia,*
[2]*Institut of Mineralogy and Petrology, Faculty of Sciences, University of Zagreb, Croatia,*
[3] *Croatian Geological Survey, Sachsova 2, 10000 Zagreb, Croatia,*

Abstract: This paper presents the research results of the presence of the rare elements Rb, Sr, K и Pb in the soils of the Tikvesh area (Republic of Macedonia) which are obtained through the XRF-method, then, their spatial distribution is presented through the analysis of the analytical data with the cringing method, and conclusions are made for the connection between the spatial distribution and the studied elements with the geological processes which happened on this area. The statistical parameters which refer on the distribution of the research elements are: (K), Mean-1.792%; Variance-0.1190;SD-0.3449; RSD-0.1925; SEM-0.0370; Median-1.810; Minimum-0.700; Maximum-2.650; (Rb), Mean-107.994 ppm Variance-566.96;SD-23.81; RSD-0.2205;SEM-2.5528;Median-109; Minimum-38; Maximum-156;(Sr), Mean-227.43ppm; Variance-14617;SD-120; RSD-0.5316; SEM-12.96;Median-191; Minimum-100; Maximum-790; (Pb),Mean-17.798ppm; Variance-124; SD-11.15; RSD-0.6196;SEM-1.1955; Median-14.400; Minimum-4.600; Maximum-55.800; The studied elements K, Rb, Sr,Pb are with similar spatial geo-chemical distribution which is linked with the existence of the soil type- litho soils which developed through the volcanic materials (tuffs and volcanic agglomerates).Only the Pb has one more maximum on its geochemical distribution (in some parts of the towns of Kavadarci and Negotino) which is linked with a long-term usage of the fuels which contain lead.

Introduction

Rb abundance in the major rock types reveals it geochemical association with Li, and therefore it has higher concentrations in acidic igneous rocks and sedimentary alumino-silicates. In weathering, Rb is closely linked to K. The behavior of Rb in sedimentary and pedogenic processes is controlled mainly by adsorption on clay minerals (Franz and Carlson, 1987). The Rb content of soils is largely inherited from the parent rocks, granites, andezites, quartzlatites, gneisses (100 to 120 ppm). The lowest mean Rb concentrations (30 to 50 ppm) are in the organic soils (Shacklette and Boerngen, 1984). Rb means for soils of various countries range from 33 to 270 ppm as given by (Wedepohl, 1969/74).

Sr is a relatively common trace element in the rocks of the continental crust and is likely concentrate in intermediate magmatic rocks (diorites, andesites) and in carbonate sediments. Sr is easily mobilized during weathering, especially in oxidizing acid environments, and then it is incorporated in clay minerals and strongly fixed by organic matter. Sr contents in soils are highly controlled by parent rocks and climate, and therefore its concentrations range in surface horizons from 715 to 1000ppm (Govindaraju, 1994).

K is widely distributed throughout the Earth's crust and is likely to be concentrated in acidic igneous rocks and sedimentary alumino-silicates. The concentration of the K in the surface horizons of the soils are in the percentage range and are closely connected with the petrology of the parent rocks (granites, gneisses, andesitic, latites).

The terrestrial abundance of the Pb indicates a tendency for Pb to concentrate in the acidic series of magmatic rocks (10 to 40 ppm). The average abundance of Pb in the Earth's crust is estimated at about 15 ppm. The natural Pb content of soil is inherited from parent rocks. However, due to widespread Pb pollution, most soils are likely to be enriched in this metal, especially in the top horizon, over 100 ppm (Davies, 1977).The natural Pb occurrence in top horizons of different soils from various countries show that amounts range from 3 to 189 ppm, average 32 ppm.

Geography, geology and pedology of Tikves area

Among the valleys in Macedonia, which by their position differ from one another, the Tikvesh Valley stands out as a separate geographical entity with its geo-morphological anthropo-geografical characteristics. With an area of 2120 km2 the Tikves area occupies a significant part of the territory of Macedonia. The Tikvesh valley is surrounded by mountains: on the south are the Mariovo Magelanski mountains, whose ranges are up to 1700 meters. The mountain heights to the east and west are also well expressed. On the west is the mountain valley "Borila" of 1500 meters and on the south is thee mountain "Ballina" with 1400 sq and "Karadaku" with 750 meters height. Thus framed among the mountains, the Tikvesh valley on the north side is cut from the river Vardar, on the west side from the Crna River and through the valley passes the river Luda Mara passes.

In a narrow geographical sense, the Tikvesh valley lies in the north basin of the river Bregalnica facing the villages Vinichani and Nogaevci and then turns over the villages of Gradsko and Dolno Chichevo , and then over Sirkovo, Mrzen, Oraovec, Farish and Raec villages, to the hill village Nikodin and the hill Nozot to the the village Toplice (Fig.1)

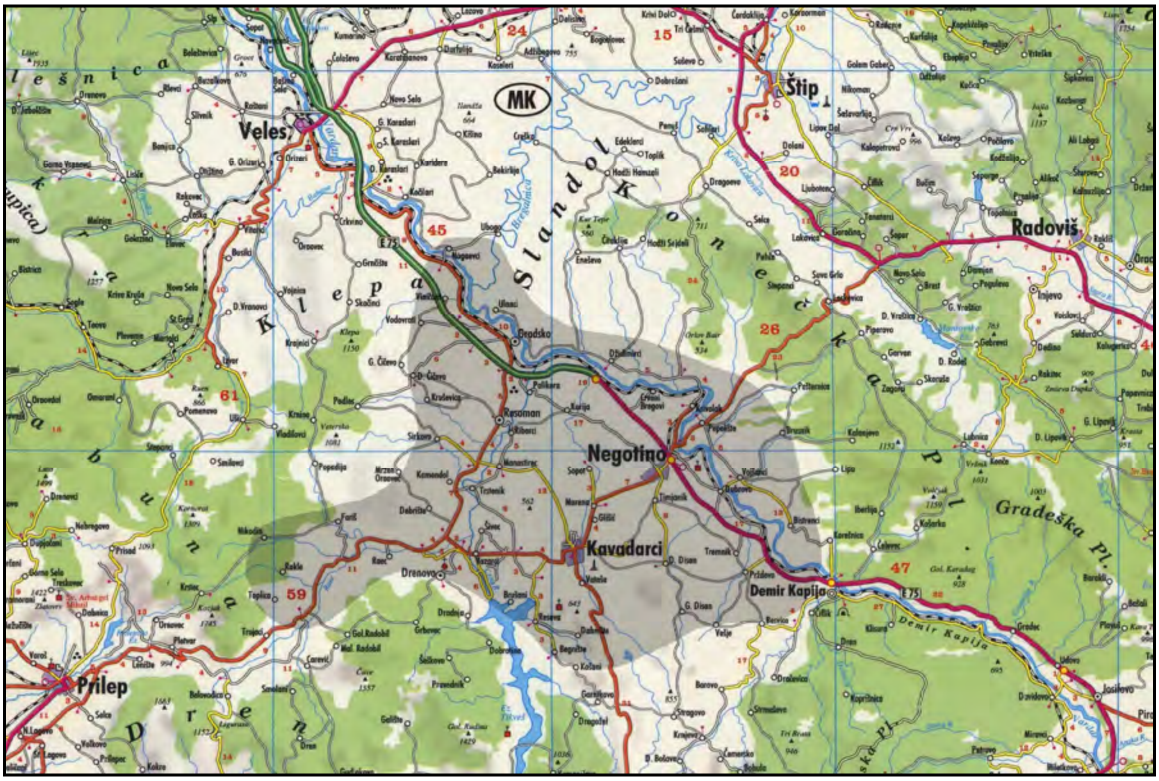


Fig.1. Geographical map of Tikves area

The western border of the valley starts from the locality Toplica through the road Gradsko-Prilep to the villages Raec and Drenovo towards the Tikvesh Lake. It encompasses the areas of Suva Gora and the villages Begnishte, Koshani and Dabnishte. On the south, the area continues to the villages Vatasha, Moklishte and the Vitacevo plateau. In this part the area Belgrad with the villages Gorni and Dolni Disan, Przdevo and Demir Kapija are encompassed. The south side ends with the village Dren.

The east side goes across the river Vardar in the direction of the village Koreshnica, then cuts the Lipkovska river and go towards the villages Brusnik and Pepelishte, crosses the Vardar river and the railway line Skopje-Gevgelija to the village Ulanici and ends with the mouth of the rivers Vardar and Bregalnica.

The geological characteristics of the area Tikvesh has been the subject of research by a large number of geologists, yet the most complete description can be found in the works of Rakićević and associates (1965) and Hristov and his associates (1965). On the basis of these studies which are made within the elaboration of the Basic geological map of the Republic of Macedonia in Tikvesh area the litho stratigraphic sequence has the following order (Fig.2).

The oldest formations are headed in a northwest-southeast direction (NW-SE) and they belong to the inner part of the Vardar zone. The lowest Paleozoic (Pz) metamorphic complex is represented by two series as follows: a series of amphibole and amphibole-chlorite shists with layers of marble and a series of quartz-shists with layers of marbles and pylons. Among the layer structures in the Vardar zone in the form of elongated tapes and interspersed lenses appear the serpentines. The southwest end of the Tikvesh area is presented with marbles and dolomites, which are probably of Devonian age.

Through a series of Paleozoic metamorphic rocks the Mesozoic (Mz) formations are developed, mainly from Late Cretaceous age. The Turonian (K2) sands, the conglomerates and the massive lime stones are spread towards the south-west and the west part of the Tikvesh area. The diabases and the submarine outbursts of spilites are common in the lower parts of this sequence, where also appear smaller masses of gabbros. The Paleozoic and the Mesozoic rocks cover almost 39 km2 in the southwest and west of the area Tikvesh.

The complex of Tertiary and Quaternary sediments covers much of the area Tikvesh. The upper Eocene (4E3) flish sediments and yellow sands occur along the valleys of the rivers Vardar, Crna and Luda Mara, and in a fraction of the Tikvesh pool. These sediments are with depth of up to 3500 m and cover about 34 km2 mainly in the northern part of the Tikvesh area.

The Tikvesh basin is filled with Pliocene (Pl) sediments, bordering the Vardar River in the north, and the Paleozoic-Mesozoic formation, which is spread on the north-west-southeast. This area is mainly represented by series of different sands. These series are homogeneous, and they contain mostly yellow sand with a low content of coarse sandy clay (pebble sandy clays) and fine gray sandstone, poor in fossil remains. Pliocene (Pl) sediments cover most (about 182 km2) of the central part in the Tikvesh area.

Southeast of Kavadarci there were Quaternary (Q) pyroclastic vulcanites with tuffs, Brecias and agglomerates, which covered around 25 km2.

The quaternary period is represented by diluvium (d), river terraces (t) and alluvium (al). The diluvial sediments (12 km2) contain coarse material from the surrounding rocks, mixed with sand and clay material. Along the rivers Vardar, Crna and Luda Mara terraced sediments are formed (23 km2). The terraces contain gravel, sand and clay. The alluvial sediments (40 km2) cover the flooded plains of the rivers Vardar, Crna and Luda Mara and contain mainly sand and clay.

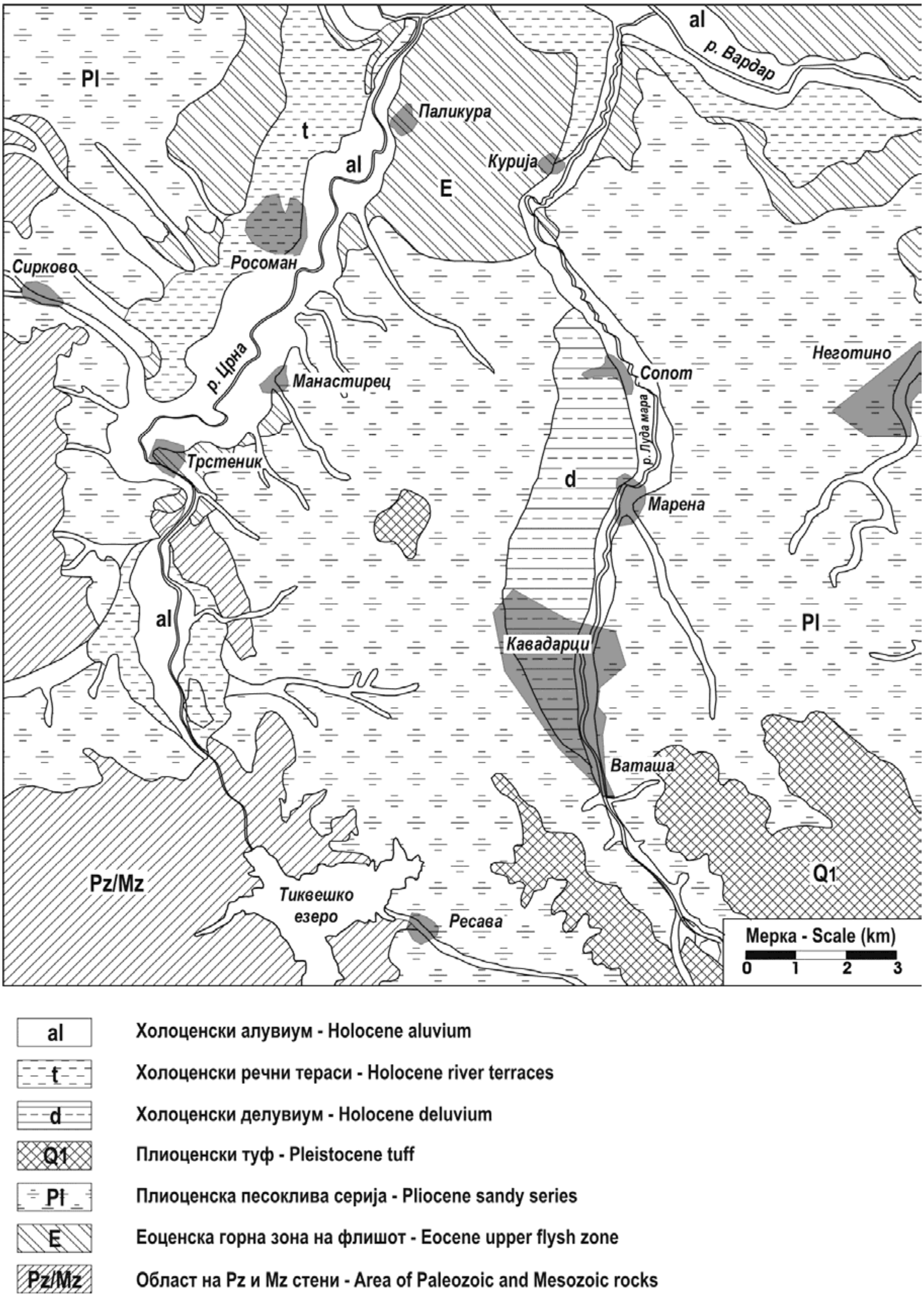


Fig.2. Geological map of Tikves area

The pedogenetic features of the Tikvesh area are shown on the basis of the pedological description of the present types of soils (Fig.3):

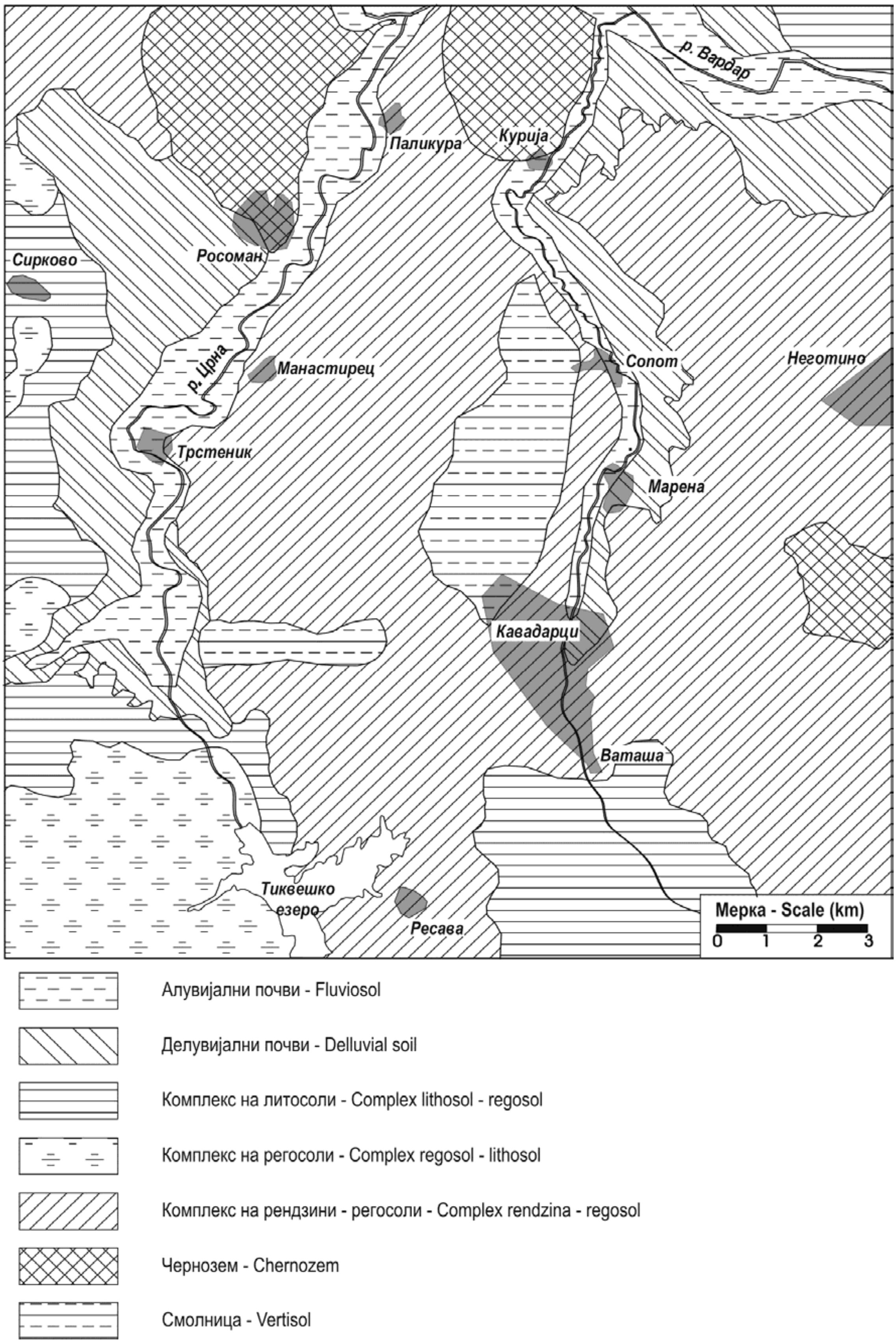


Fig.3. Pedological map of Tikves area

The litosols from the type (A)-R1-R2 are developed or poorly developed soils with a maximum depth of 20 cm of the solum, and they are formed of solid or low-cracked rock. These soils have a low productive capacity due to the shallow solum, the high skeleton content and the low content of clay. These soils have no importance for the agricultural production.

The regosols from the type (A)-C, are formed of bulk sediments. They are formed by accelerated erosion of the soil profile of previously developed soils with initial pedogenetical processes which lead to the creation of poorly developed horizon (A). These soils are susceptible to erosion, so we recommend anti erosive safety measures. The regosols are characterized by lower fertility than the soils from which they incurred by erosion.

Soil complex from regosols and litsols in the Tikvesh area appear in fields that are characterized by higher slope, west of the Tikvesh Lake in the areas of the villages Debrishte , Kamen Dol and Krusevica and northwest to the village of Dolno Chichevo.

Soil complex of litosols and regosols and renzines are often observed. The lithosols are seen on the highest parts of the terrain. Very often on the surface where there is a presence of lithosols, the appearance of solid rocks is noted. The regosols appear on the fields that are characterized by a slightly greater slope where erosion by the solum is younger, whereas the rendzines appear on the flatter terrains in foot of the hills where the phenomenon of the often change of the regosols is noted even at small distances. This soil complex is spread around the village Drenovo, then in the villages Sirkovo, Kamen Dol Mrzen Oreovec, and Debrishte and on the east of Gradsko on the left side of the river Vardar.

Soil complex litosols and regosols and rankers appear at the plateau Vitachevo near Kavadarci. The lithosols and the rankers are formed on the basis of compact volcanic tuffs whereas the regosols are form from erosion of the humus accumulative horizon of the rankers.

The diluvial (colluvial soils) are defined as underdeveloped and poorly developed soils with the possible (A) or Ar horizon. They have a simple construction of the profile of type (A)-C. They are formed through erosion and transportation of the substrates and the soils of the higher terrain with surface water and water from torrential streams and modern sedimentation of such eroded material in the footer parts of the terrain. The horizon (A) contains a slightly larger amount of humus than the horizon (C), but there are no visible signs of the formation of structural aggregates. The diluvial soils have large horizontal and vertical (in depth profiles) heterogeneity of all properties. In comparison with the alluvial soils with which they border, they have lower productive capacity.

Renzines are soils with profile from the type-A-AC-C. They are formed on the bulk silicate carbonate substrate with molic horizon. The depth of the humus horizon is 40 cm; it has a dark blue, dark brown to black color with well-articulated structure. The carbonates rise from surface or at a lower depth. Mostly the renzines are extensively used in the agriculture and one part of them is under pastures. The map is represented as a complex of rendzines, rego salts and litho salts. The complex of rendzines and regosols occupies the largest part of the Tikvesh area. In the vicinity of the village of Dolno Chichevo appear small areas cement forest soils and regosols.

Resins are loamy soils formed over clay sediments with more than 30% of clay, which gives them a capacity of swelling (smektites) or on basic rocks and ultra basic rocks with which decay larger quantities of clay are obtained. The resins in Tikvesh area developed over tertiary sediments of clay, low wave relief with a little slope. They have the type of profile A-AC-C. The soil contains more than 30% clay and the horizon A has vertical properties: cracks and typical prismatic structure. The horizon A has a depth greater than 30 cm and AC and is typically 20-30 cm deep. In the Tikvesh area the places under resins are set aside as an independent soil type. They are prevalent in the vicinity of the villages Ribarci, Trstenik and Vozarci and north of Kavadarci.

Chernozem is a soil type of the semiariditic steppe regions with typical molic A0 horizon that is thicker than 40 cm and with a front horizon AC (25-30 cm). It contains CaCO3 mostly of the surface and the lower part of horizon A or AC. The horizon A has well expressed stabile grain structure. In the Tikvesh area, the chernozems often contain carbonates from the surface, and in some parts of the profiles they are washed to a certain depth of the solum. The chernozems are segregated as separate pedological units (Fig.) north of the village Rosoman and smaller areas are located east of the village and between villages Palikura Timjanik and Dolni Disan.

The cement forest soils are soils with a profile of the type Ar-(C) or Ar-S-(C) S-S. They are characterized by cambic horizon (B), which lies between A and C horizons. The cambic horizon (B) always contains more clay than the A horizon. it is more compressed with reduced capillary limpidity, reduced stability of the structural aggregates and reduced water resistance. The production capacity of these soils is not great.

The alluvial soils are modern (recent) river or lake sediments of layers, and they can have both horizons (A) or (Ar), and even G. Unlike the diluvia soils they are characterized by good sorting. The suspended materials from which these soils have formed have heterogeneous mineralogical-petrographic composition. According to the mechanical properties they are light soils. The macro structure is poorly expressed, and therefore the physical properties depend on the mechanical composition. They have good water, air and heat mode. These are very fertile soils and the agricultural production is intensive over them. They are represented as a single soil type along the rivers Vardar, Crna and Luda Mara.

Applied methodology of work

The applied methodology of works consist of terrain and laboratory work. During the terrain work 87 samples of soils are collected (top soil) with a depth of sample from 15 cm. The quantity of each sample is 2 kg and they are collected in the uncultivated agricultural fields. Each sample is documented with PPS and for each sample the coordinates (X, Y, and Z) are taken. The so collected soil samples are dried and sprinkled with a 2 mm colander, and represented samples are taken for a further elaboration which was sprinkled on 74 microns. The determination of the presence of the elements in traces is made with the XRF method at the University of Zagreb. The obtained results are analyzed with the criging method and the geochemical maps are drawn for the distribution of all the determined elements.

Obtained results and discusion

The obtained results from the laboratory research together with the statistical parameters are shown in the Table 1.

The analyzed data shown on the geochemical maps for distribution of the elements point ot he fact that Rb, Sr, K and Pb are with a very similar geochemical distribution in the area which is a subject of research. The contents of Rb are from 38.6 to 156.9 ppm or an average value of 108 ppm.

Table 1. Basic statistical parameters

Elements	N	Mean	Variance	SD	RSD	SEM	Median	Minimum	Maximum	Normal Distr.
Al (%)	87	12,402	4,1191	2,0295	0,1636	0,2176	12,220	9,880	27,300	0,000
As (ppm)	87	10,091	12,4169	3,5238	0,3492	0,3778	10,300	3,100	30,000	0,000
Ca (%)	87	5,043	10,0002	3,1623	0,6271	0,3390	4,510	0,580	12,360	0,042
Co (ppm)	87	15,839	3,8185	1,9541	0,1234	0,2095	15,500	12,600	23,200	0,000
Cr (ppm)	87	194,609	5997,2839	77,4421	0,3979	8,3027	182,900	107,500	630,000	0,000
Cu (ppm)	87	60,467	4411,7492	66,4210	1,0985	7,1211	46,800	28,100	627,300	0,000
Fe (%)	87	3,971	0,3955	0,6289	0,1584	0,0674	3,859	2,948	6,242	0,000
Ga (ppm)	87	16,410	8,3258	2,8855	0,1758	0,3094	16,000	10,400	23,100	0,186
K (%)	87	1,792	0,1190	0,3449	0,1925	0,0370	1,810	0,700	2,650	0,016
Mn (ppm)	87	1085,143	1138154,2811	1066,8431	0,9831	114,3776	917,600	225,800	10558,200	0,000
Ni (ppm)	87	113,129	2149,4353	46,3620	0,4098	4,9705	103,700	57,600	449,300	0,000
Pb (ppm)	87	17,998	124,3488	11,1512	0,6196	1,1955	14,400	4,600	55,800	0,000
Rb (ppm)	87	107,994	566,9678	23,8111	0,2205	2,5528	109,700	38,600	156,900	0,411
Sr (ppm)	87	227,439	14617,1415	120,9014	0,5316	12,9620	191,900	100,800	790,600	0,000
Ti (ppm)	87	4311,884	307414,4865	554,4497	0,1286	59,4432	4270,770	3164,480	5715,200	0,252
Tl (ppm)	87	0,628	0,0638	0,2525	0,4020	0,0271	0,580	0,290	1,530	0,000
V (ppm)	87	116,352	390,0453	19,7496	0,1697	2,1174	114,800	84,400	197,300	0,000
Y (ppm)	87	67,309	343,3722	18,5303	0,2753	1,9867	68,700	24,700	106,300	0,383
Zn (ppm)	87	124,361	1542,2724	39,2718	0,3158	4,2104	117,200	90,600	423,100	0,000
Zr (ppm)	87	302,314	39366,5679	198,4101	0,6563	21,2718	292,800	2,400	862,200	0,003

The increased concentrations of Rb (over 100 ppm) coincide with the lithological formation shown with the pyroclastical rocks, and through which the lithosoils are developed (Fig.4). Thus, it can be concluded that the concentration of Rb in the soils of the Tikvesh area have no anthropogenic origin and that they are within the frames of the published values for such geological and pedological formations (Stafilov at all.2008).

The concentration of Sr is from 100.8 to 790.6 ppm or with an average value of 227.4 ppm (Fig.5). These concentrations of Sr are in the limits of the published values for natural distribution of Sr in different countries in the world (Duddy, 1980; Shacklette et all, 1984; Tjell et all, 1972).

The shown data in Table 1 and Fig.6. point to the fact that the concentration of K in the studies samples of the soils of the Tikvesh area is in the interval from 0.70 to 2.65 % or an average value of 1.79 %. These values are very close to the values published for these type of soils (Stafilov at all.), and from the shown geochemical distribution (Fig.6) it can be concluded that this is about a natural geochemical distribution which is strictly controlled with the geological type of the soil.

The concentrations of Pb are from 4.6 to 55.8 ppm or an average value of 18.0 ppm and these values are very close to the values which are published for the concentration of Pb in the soils in various parts of the world (Kabata-Pandias, 1981; Rauta et all, 1985). The values which are obtained for the concentration of the Pb in the soils of the Tikvesh area are very close to the published results (Stafilov et all.)

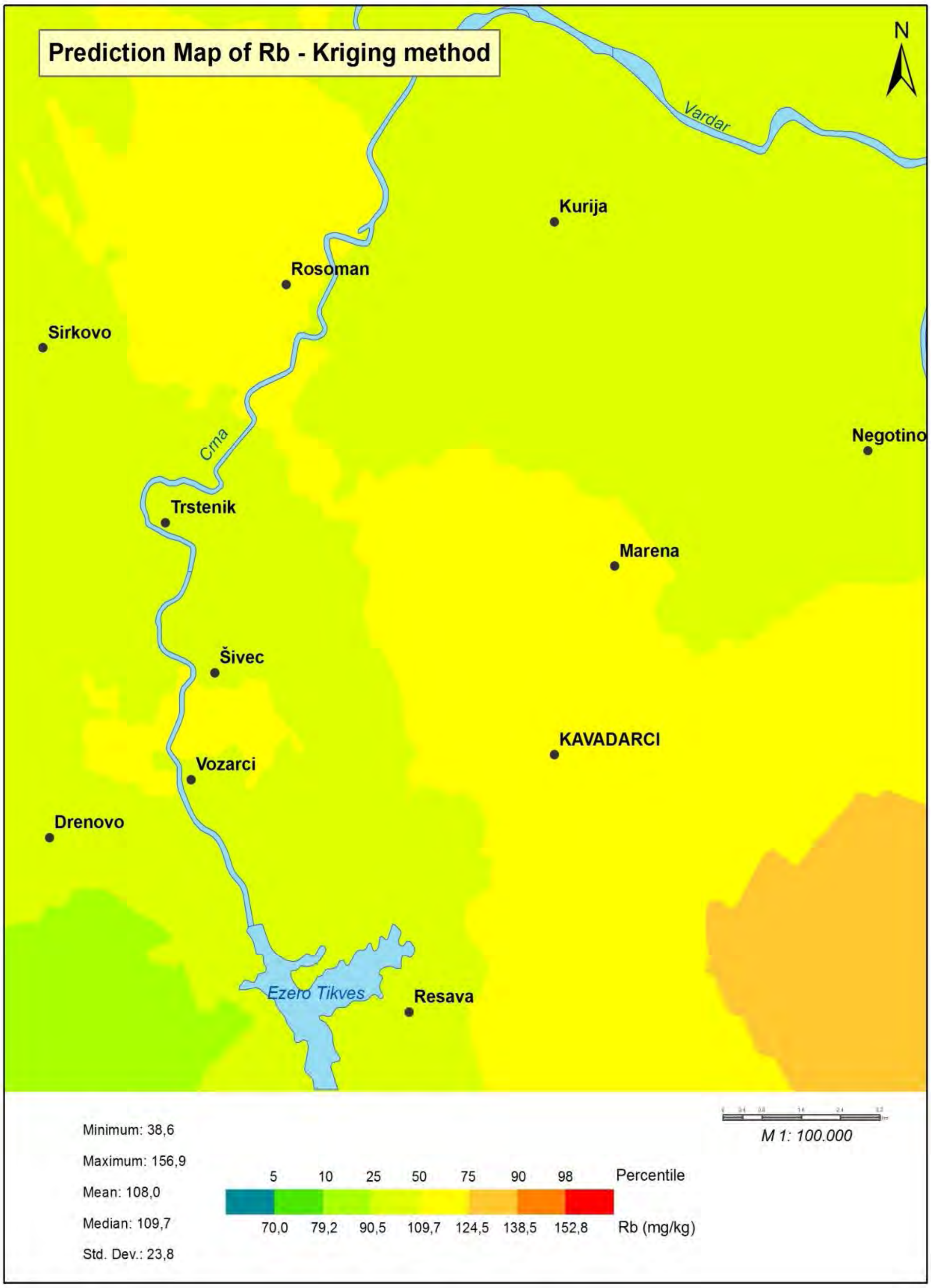


Fig.4. Distribution map of Rb in the soils of Tikves area

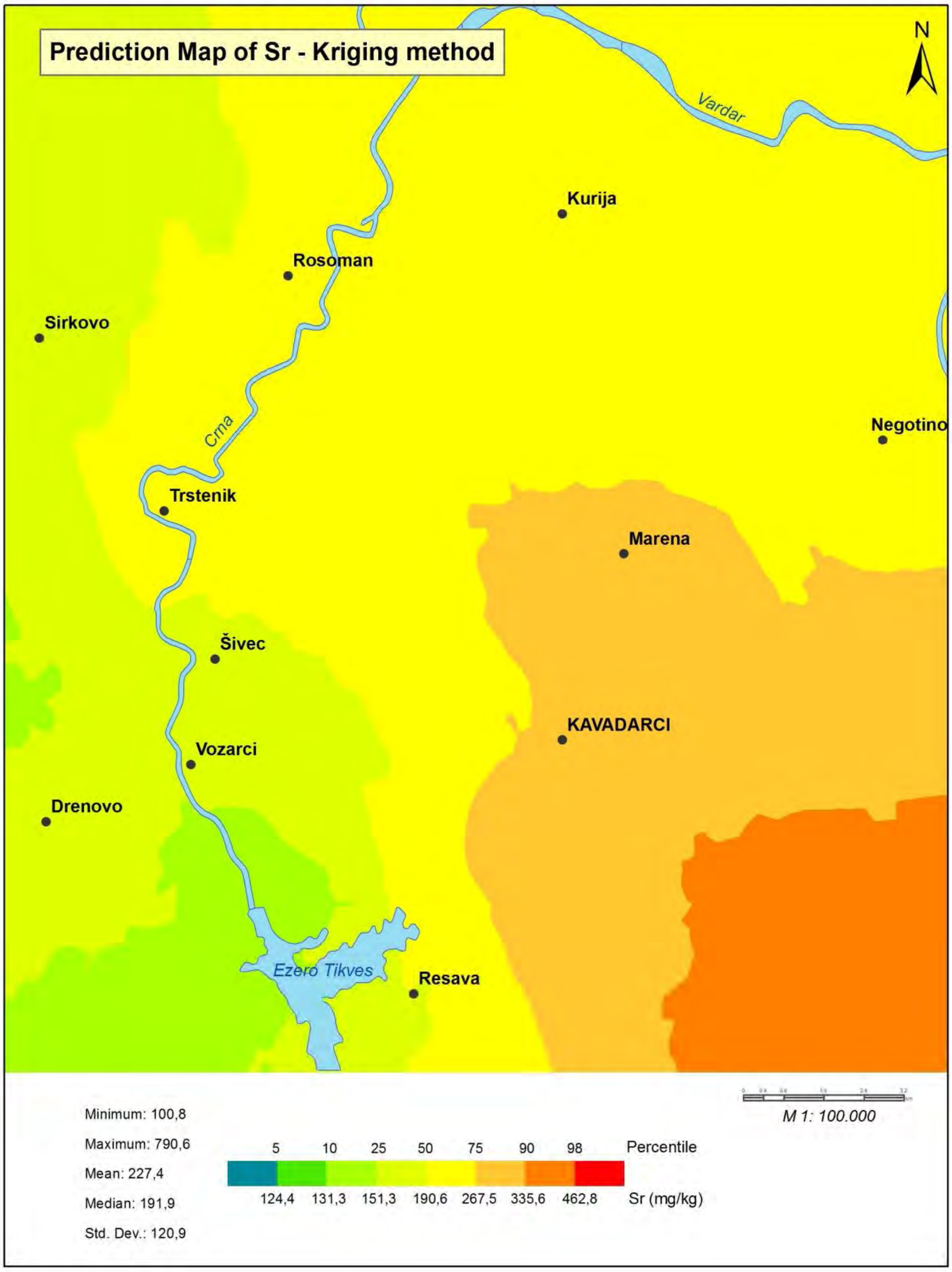


Fig.5. Distribution map of Sr in the soils of Tikves area

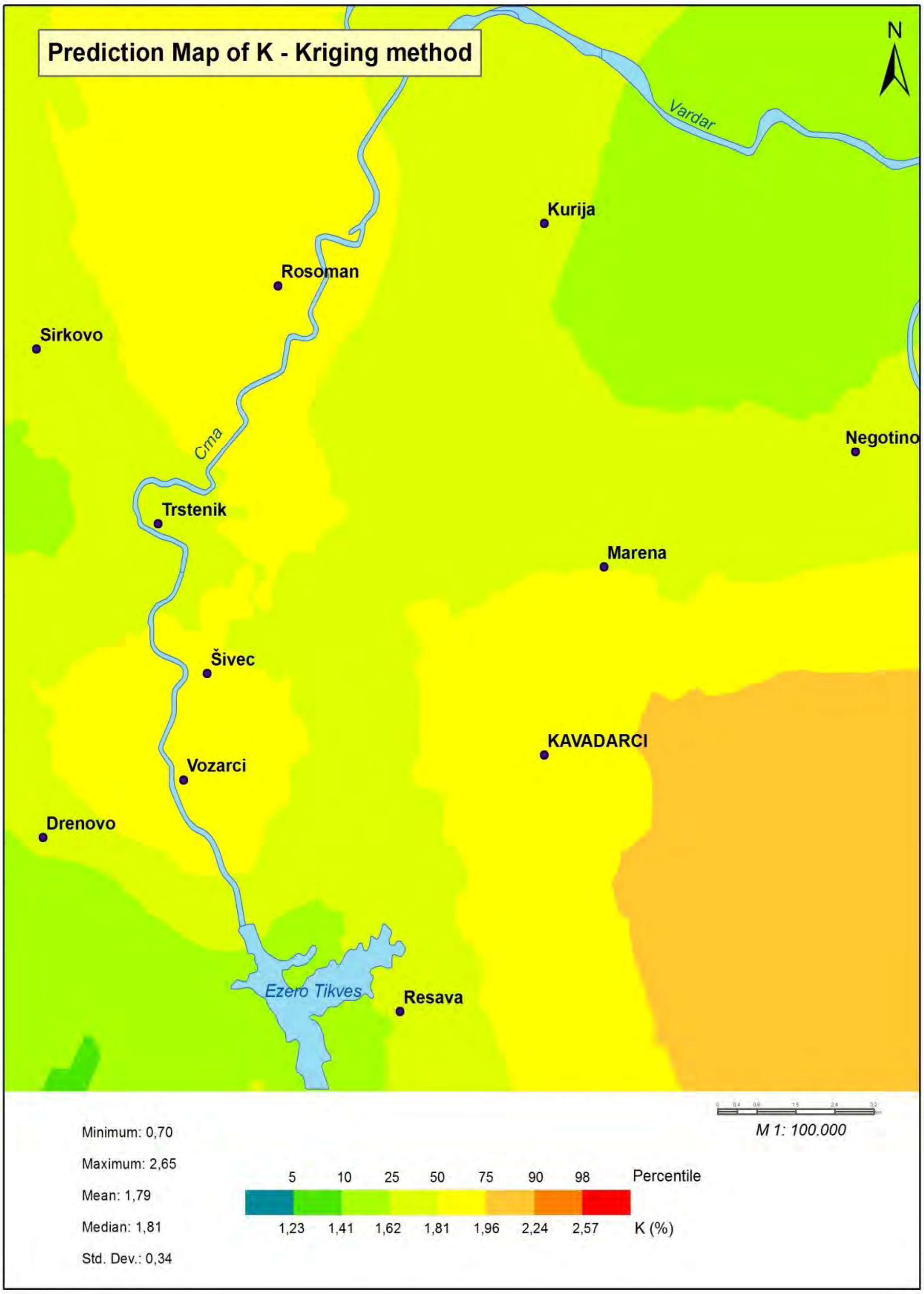


Fig.6. Distribution map of K in the soils of Tikves area

Also, from the (Fig.7) it can be concluded that the maximum which appears in the regions of the towns Kavadarci and Negotino is a result of the small anthropogenic influence which is present at the cars during the incineration of the fuels which contain lead.

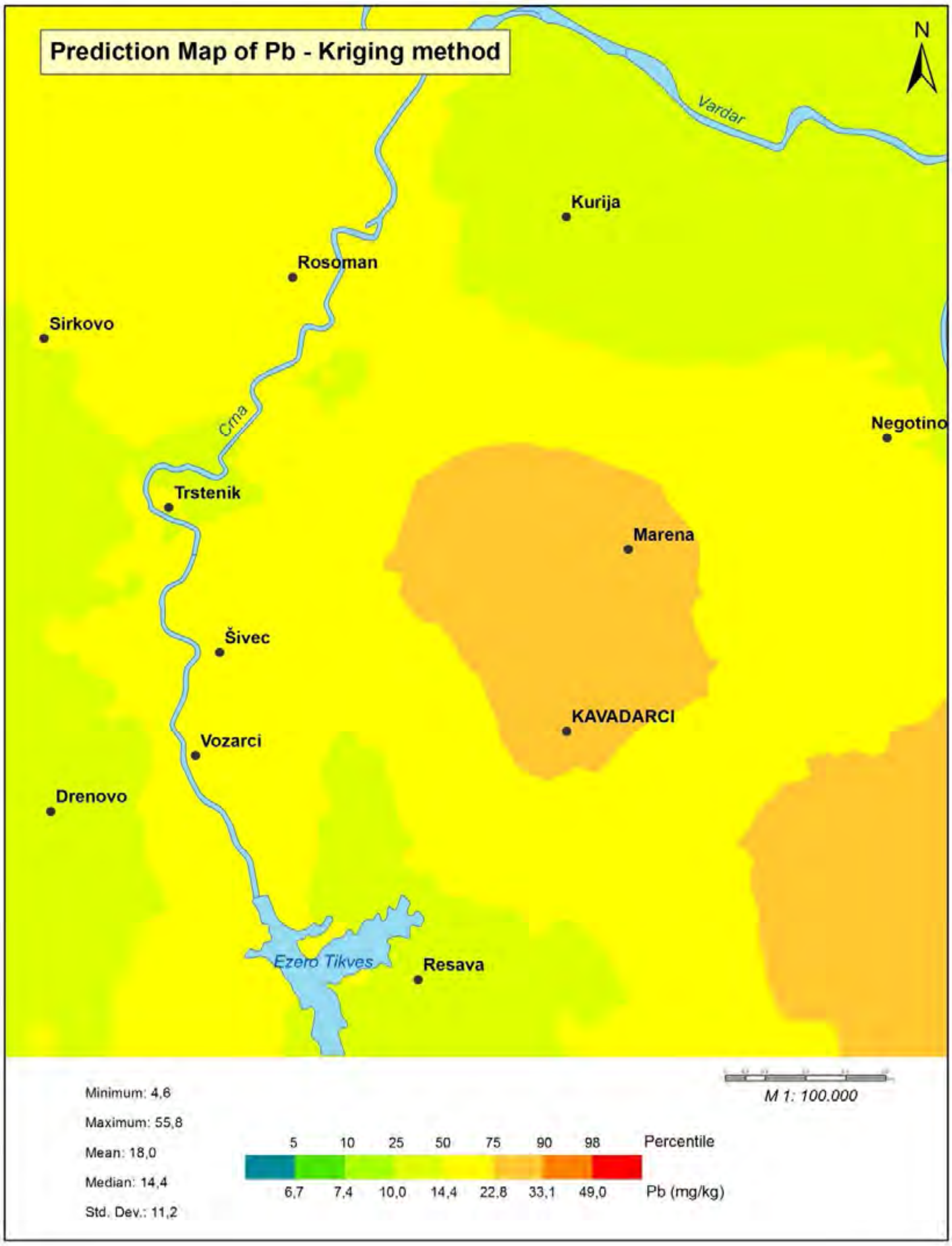


Fig.7. Distribution map of Pb in the soils of Tikves area

Conclusion

The obtained results for the concentrations of Rb, Sr, K и Pb in the soils of the Tikvesh area point to the fact that these elements have very similar geochemical distribution in the research area. The type of the geochemical distribution leads to the conclusion that this is about a natural geochemical distribution with a very little influence of the anthropogenic factor (only in the case of Pb in the nearby of Kavadarci and Negotino). The maximum concentrations of Rb, Sr, K, Pb coincide with the development of the soil type litho soils through the pyroclasstic rocks which are present in this region.

Referencess

Davies, B. B., Heavy metal pollution of British agricultural soils with special reference to the role of lead and copper mining, in Proc. mt. Semin. on Soil Environment and Fertility Management in Intensive Agriculture, Tokyo, 1977, 394.

Duddy, I. R., Redistribution and fractionation of rare-earth and other elements in a weathering profile, Chem. GeoL, 30, 363, 1980.

Franz, G. and Carlson, R. M., Effects of rubidium, cesium and thallium on interlayer potassium released from transvaal vermiculite, Soil Sci. Soc. Am. J., 51, 305, 1987.

Govindaraju, K., Compilation of working values and sample description for 383 geostandards, Geostand. NewsletL, 18, 1, 1994.

Hristov, C, Karajovanovic, M., Strackov, M., 1965: Basic geological map of SFRJ, sheet Kavadarci, M 1:100,000 (map & interpreter), Fedaral Geological Survey, Beograd, 62, pp.

Kabata-Pendias,A., Heavy metal concentrations in arable soils of Poland, Pamiet, Pulawski, 74, 101, 1981 (P0).

Shacklette, H. T. and Boerngen, 5. G., Element concentrations in soils and other surficial materials of the conterminous United States, US. GeoL Sun'. Prof Pap., 1270, 105, 1984.

Wedepohl, K, H., Ed., Handbook of Geochemistry, Springer-Verlag, Berlin, 1969—1974 (several volumes).

Rakicevic, T., Stojano, R., Arsovski, M., 1965: Basic geological map of SFRJ, sheet Prilep, M 1:100,000 (map & interpreter), Fedaral Geological Survey, Beograd, 65, pp.

Rauta, C., CUrstea, S., and Mihäilescu, A., Influence of some pollutants on agricultural soils in Romania, Arch. Ochr~ Srodowiska, 33, 1, 1987.

Stafilov, T., Sajn, R., Boev, B., Cvetkovic, J., Mukaetov, D., Andreevski, M., 2008: Geochemical atlas of Kavadarci and the Environs, Faculty of Natural Sciences and Mathematics, Skopje

Tjell, J. Ch. and Hovmand, M. F., Metal concentrations in Danish arable soils, Acta Agric. Scand., 28, 81, 1972.

PARTICULAR MACEDONIAN TERTIARY BASINS: GEOLOGICAL FEATURES AND ANTHROPOGENIC INPUT

Todor Serafimovski[1], Tadej Dolenec[2], Goran Tasev[1], Nastja Rogan-Šmuc[2], Matej Dolenec[2], and Petra Vrhovnik[2]

[1]*Faculty of Natural and Technical Sciences, University "GoceDelcev"-Štip, Macedonia*
E-mail addresses: todor.serafimovski@ugd.edu.mk; goran.tasev@ugd.edu.mk
[2]*Department of Geology, Faculty of Natural Sciences andEngineering, University of Ljubljana, Slovenia*

Abstract: The most important Neogene basins from the anthropogenic input point of view of are: Skopje, Slaviski, Kocani, Lakavica, Veles and Tikves basin. These basins were subjected to an environmental study and observations within the study, which results are given in this paper. Within all the aforementioned basins were determined significantly increased concentrations of particular heavy metals such as: Cu, Pb, Zn, Ni, Cd, Mn, Mo etc., as a direct consequence of processes introduced by human activities.

Key words: Pollution, Tertiary basins, Macedonia, anthropogenic, heavy metals

Introduction

Macedonia lies within the Cenozoic Southern BalkanExtensional regime that forms the northern part of the more regional Aegean extensional regime. Study of thelate Cenozoic basins of Macedonia provides important data that contributes to the unravelling of the tectonic evolution of the Southern Balkan extensional regime (Burchfiel et al., 2000, Nakov et al., 2001).The Cenozoic tectonic evolution of Macedonia consists of two periods of extension, the earlier in Paleogene time and the later in Neogene time, separated by two episodes of shortening. Paleogene extension and related basin development was diachronous and began in late Eocene time and continued into early Oligocenetime. The Paleogene basins trend generally NW-SE and were formed mainly within the Vardar zone and Serbo-Macedonian tectonic units. They are filled with Eocene-Oligocene molassic sediments, which reach a thickness of 3500–4000 m and can be divided into five lithologic units that are paleontologically well-dated. The second period of extensional deformation in Macedonia, which continues to present day, began in early to middle Miocenetime and is marked by the deposition of middle Miocene stratain the deepest basins. The beginning of extension in Macedonia is contemporaneous with widespread extensional deformation throughout the central Balkan Peninsula (Zagorchev, 1992;Burchfiel et al., 2000; and Nakov et al., 2001). Late Cenozoic extension and associated basin formation is characterized by differential vertical tectonic motions related to normal, oblique, andstrike-slip faulting.

Tertiary basins in the area of the Republic of Macedonia have been populated by human population, which left marked traces of their life.Anthropogenic effects as an integral part of so called anthrosphere may be defined as that part of the environment made or modified by humans and used for their activities. Natural characteristics such as sufficient arable land, ground waters, provided good conditions for the development and advancement of civilisation there. On the other hand, the close proximity of the basins to the folded mountainous regions in which (particularly in the Tertiary) numerous metallic ore deposits formed provided favourable conditions for the development of mining and metallurgy. Traces of these mining activities speak for activities that are older than 2000 years that have continued to the present time with different intensity. The intense development of human settlements resulted in enormous consequences on the human environment and increased concentrations of some pollutants in the air, soil and water. These phenomena have an impact on the human, plant and animal population in a non-reversible manner. Some of the anthropogenically introduced pollutions we are giving in the text below.

NEOGENEBASINS IN THE REPUBLIC OF MACEDONIA AND ANTHROPOGENIC POLLUTION WITHIN

The most important Neogene basins from the anthropogenic input point of view of are: Skopje, Slaviski, Kocani, Lakavica, Veles and Tikves basin (Figure 1).

The Skopje basin

This basin as a of the Skopje graben is bounded by a system of normal faults that strike NWSEand NE-SW to E-W. It occupies a surface area of ~550 km^{2}and the basin sediments have been studied from both well exposed outcrops and deep drill holes (that are 1655 m and 2000 m deep).Combining data from outcrop profiles, deep drilling, and some gravity studies, the total sedimentary section is ~2200–2300 m thick. The basal units of the section unconformably overlie Precambrian and Paleozoic metamorphic rocks and Upper Cretaceous sedimentary rocks. The transgressive basal conglomerate, gravel and sandstone contain clasts from the underlying rock units. Strata of all five cycles are present in the Skopje basin and are assigned to three formations of Miocene and Pliocene age and one informal unit of Quaternary age at the top.

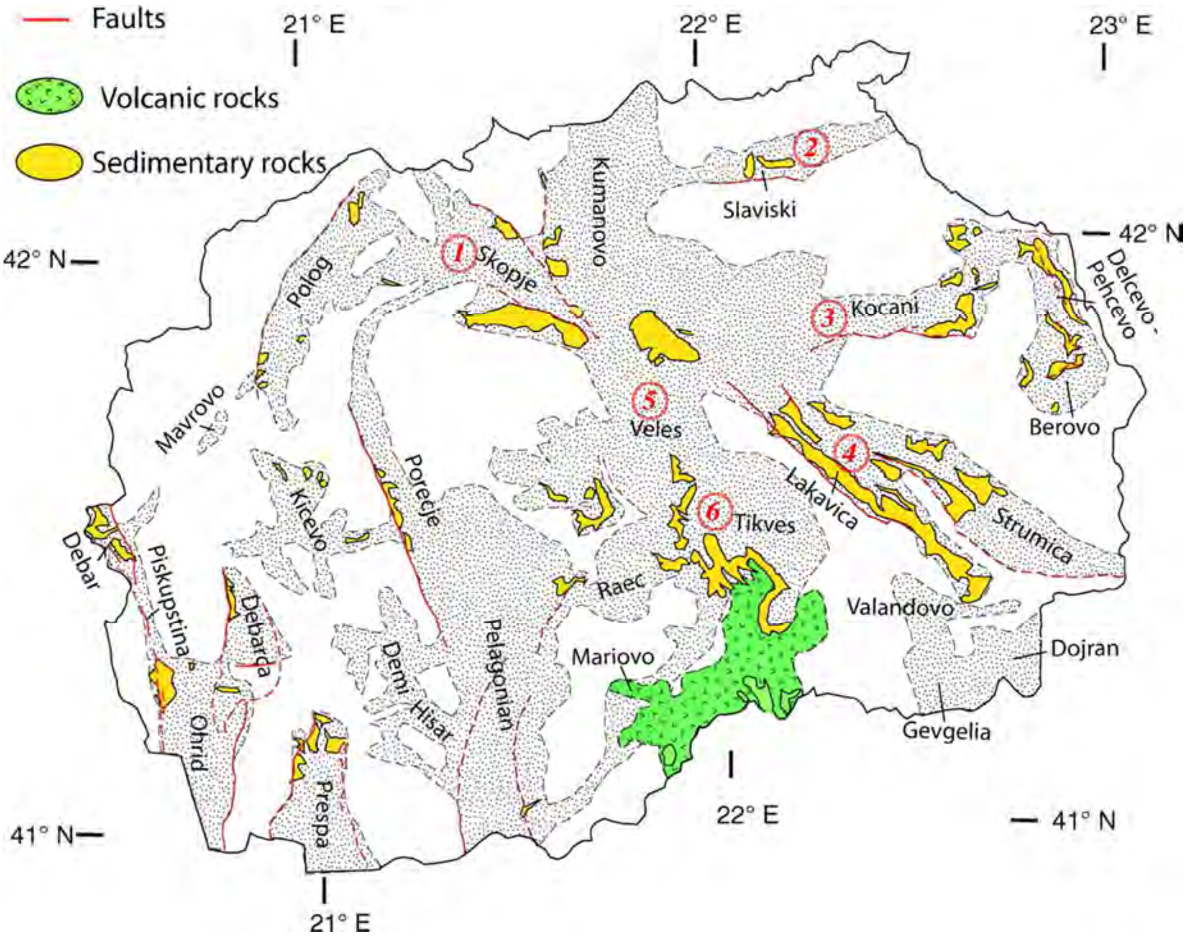


Fig. 1. Distribution of Neogene basins within the Republic of Macedonia (Dumurdzanov et al., 2005).
1. Skopje basin; 2. Slaviski basin; 3. Kocani basin; 4. Lakavica basin; 5. Veles basin; 6. Tikves basin

The *Usje Formation (UsF)* is the oldest formation and consistsof terrigenous marly strata (~1400 m thick) deposited in Badenian-Sarmatian time. This formation contains two informal lithological units from the base to the top: (*a*) an upper gravel-conglomerate unit, 50–100 m thick; and (*b*) an upper marl, marly claystone and siltstone unit, 1300–1350 m thick, that co-ntains intercalations of sandstone and rare coal beds. The second one, the *Nerezi Formation (NeF)*is partially exposed in the peripheral parts of Skopje (villages of Nerezi and Usje-Sopiste, on the highway from Saraj to Semeniste,and in the southern parts of the Skopska Crna Gora mountain). The formation is ~530 m thick and in some parts ofthe Skopje basin it rests transgressively above pre-Cenozoic rocks. Three informal lithological subdivisions are recognized, from the base to the top: (*a*) A basal gravel, sandstone and siltstone unit (~250 m thick), (*b*) A middle silty-marly coal-bearing unit that consists of~130 m of siltstone, marly claystone, marl, and coal beds, and (*c*) An upper sandy-siltstone unit that consists of interbedded yellow and grey sandstone and siltstone with gradations into silty claystone (total thickness of ~150 m). The *Solnje Formation (SoF)*was deposited above a hiatus that occurred probably after Pontian sedimentation and terminated much of the lacustrine environment in the Skopje graben.

Following the hiatus, coarse-grained sediments (gravel, gravelly sandstone, and sandstone) were depositedand indicate increased topographic relief surrounding the graben caused by an increase in activity of the graben bounding faults during Pliocene time. The sandstone and gravelly sandstone ofthe Solnje Formation is well stratified and lies above marl of the Nerezi Formation. The *Pleistocene cycle* is developed in the Skopje graben where relicts of glaciofluvial sediments are in the high parts of the surrounding mountains and travertine deposits10–20 m thick occur at many locations, such as at the villages of Svilare, Kuckovo, Matka, and Bojanek (Fig. 3). The travertine deposits lie in places above the Solnje Formation, and at other places, directly above the Nerezi Formation, but these deposits are remnants of more extensive travertine units that have been extensively eroded. In the central parts of the graben, the Pleistocene sediments locally reach 60–80 m thick and consist of alluvial gravel, sand, and sandy clay deposited by the Vardar, Treska, Lepenec, and Markova Reka rivers.

The major inhabited area within the Skopje basin is the capital of the Republic of Macedonia, Skopje. The limits of soil pollution in Macedonian capital are still to be determined. As in every large populated conglomerate in the World the pollution sources to soil are numerous and diverse. However, we have limited our research to an area adjacent to the cement producing plant Usje located on the southeastern limit of the city. The environmental awareness arise recently since in the close vicinity of the plant witnessed progressive residential area building.

In the direction of giving an initial clue about the contamination of soils around the aforementioned plant we have performed sampling along two parallel profiles and one profile perpendicular to the parallel ones. The total of 15 specimens were sampled and analyzed.

Measured values were in ranges of 1.46÷2.23% Fe, 440÷940% Mn, 93.4÷104.71mg·kg^{-1}Ni, 58.57÷83.1mg·kg^{-1}Zn, 23.1÷34.9% Pb, 42.30÷60.3 mg·kg^{-1} Cu and 0.59÷1.61 mg·kg^{-1}Cd. Also, the calculated enrichment ratio (measured values over the reference value) speaks itself regarding the level of contamination. Calculated enrichment ratios ranged from relatively low 0.98 for Fe, 1.4865 for Zn, 1.89 for Mnand 1.8975 for Pb, through 3.016 for Cu up to higher 5.92 for Cd and 7.5098 for Ni.

Obtained results served as a basis for plots construction of particular heavy metals vs. their maximally allowed concentrations in soils (Figure 2).

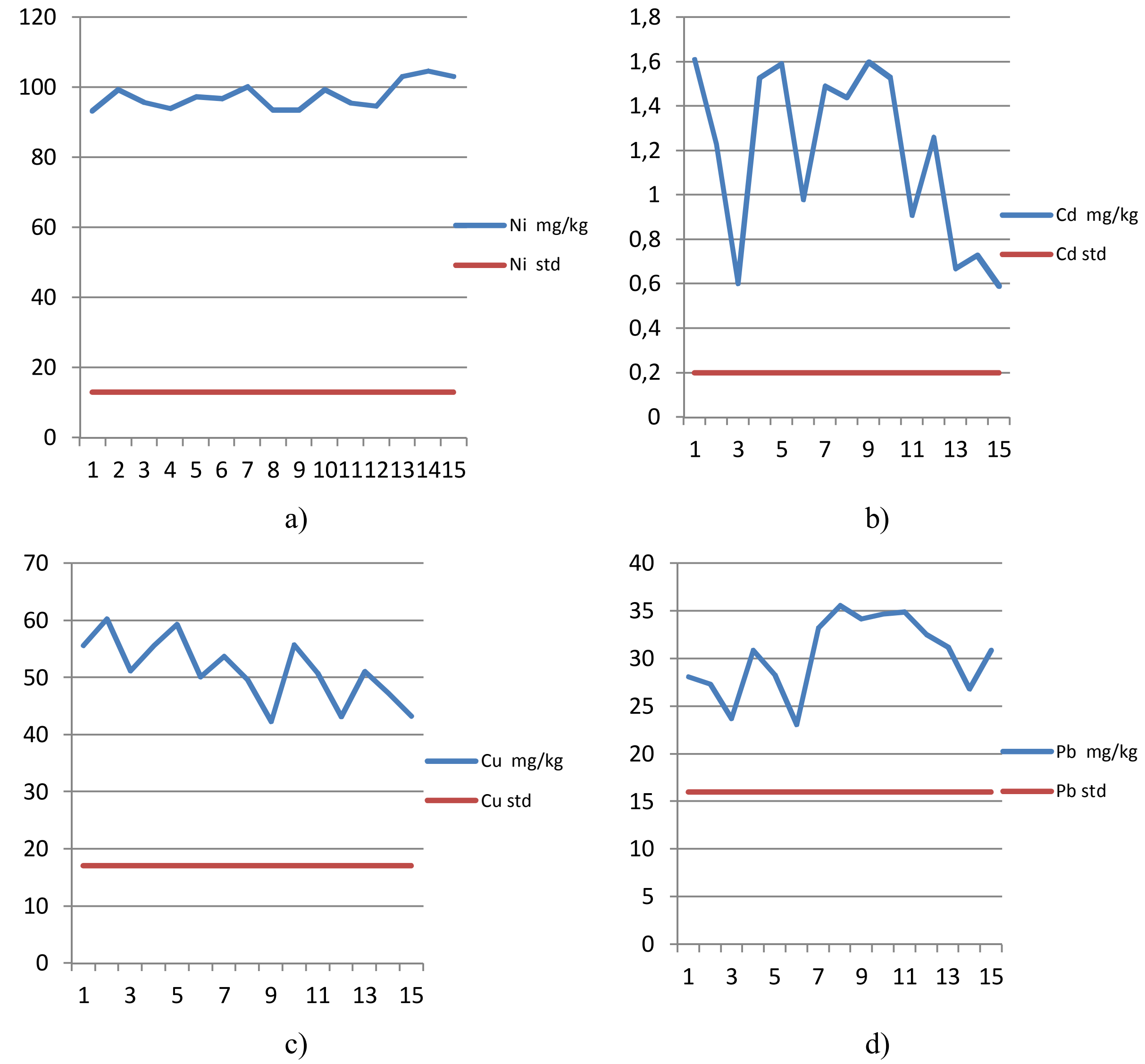


Fig. 2. Measured concentrations of some heavy metals vs. standard values around the Usje cement production plant on the city limits of Skopje, Macedonia

All the elements in all analyzed samples have shown increased values compared to the respective standard values. It was noticeable that the concentration of most of the heavy metals was the highest in samples taken from the closest vicinity of the Usje plant.

Bearing in mind sound geochemical and geological logic, the increased values should be attributed to the geological composition of the background as well as to the plant's production process and organic fertilizers used in arable areas around the plant.

The Slaviski basin

The **Slaviski basin**, which trends E-W, has a small aerial extent and thegraben is bounded on the south side by part of the steeply dipping,seismically active Kustendil-Skopje-Debar-Elbasan fault. It is composed of basinal sedimentaryand volcanic rocks in the grabens lie above metamorphicrocks of Precambrian age, sedimentary rocks of Eocene-Oligoceneage, and locally, igneous rocks of Oligocene–lower Miocene age. This major fault line strikes WSW-ENE and the thickness of strata is estimated at ~500 m. The section includes two formations and Quaternary sediments.

The *Probistip Formation (PrF)*, which is of middle and late Miocene age and is composed of two lithologicalunits (~330 mthick): (*a*) The basal marl and marly claystone, clay, tuff and sandstoneunit is ~200 m thick.(*b*) The upper unit of tuff and tuffite of andesite, latite, andquartz-latite composition is 150 m thick.

The *Ginovci Formation (GiF)*is assigned a Pliocene age based on its stratigraphic position and lithology that is similar to dated rocks in the Kumanovo graben. Its lower part consists of gravel and sandstone, and its upper part contains bentonite clay layers interbedded with sandstone, siltstone, and gravel.

The *Quaternary sediments (Q)*consist of a thin section of alluvial, proluvial, and diluvial strata.

One of the major contributors to the anthropogenic inputs into the Slaviski basin is the lead-zinc producing Toranica Mine. The mine is located approximately 18 km to the south-east of the town of KrivaPalanka and 2 km to the west of the Macedonian-Bulgarian border. No matter it is sited in a relatively remote mountain location, it still produces significant effects to the environment because the proximity of population centres and agricultural land.

Data that were reported for concentrations of metals in water samples (Alderton et al., 2005) has been augmented and confirmed by sampling of stream sediments. The contamination from the Toranica mine and its operations is visible not only at the downstream end of the tailings disposal area, but also several kilometres downstream.

Mining and processing facilities have had a major effect on the chemical composition of river sediments in the river Toranica. Concentrations of Pb, Zn, and S are each >1000 mg/kg. Although present at much lower levels, Ag, As, Bi, Cd, Co, Cr, Cu, Mn, Mo, Ni, and U are also high in the mining area.

Measured values were in ranges of 1.41÷7.90% Fe, 0.09÷0.57% Mn, 0.06÷13.47% Zn, 0.031÷4.45% Pb, 68.22÷7434.6 $mg{\cdot}kg^{-1}$ Cu, 5.98÷1026.8 $mg{\cdot}kg^{-1}$Cd, 4.99÷47.76 $mg{\cdot}kg^{-1}$Co, 23.06÷81.28 $mg{\cdot}kg^{-1}$Ni, 1.80÷58.14 $mg{\cdot}kg^{-1}$Ag, 4.13÷214.9 $mg{\cdot}kg^{-1}$As, 22.92÷56.47 $mg{\cdot}kg^{-1}$Cr. Also, the calculated enrichment ratio (measured values over the reference value) speaks itself regarding the level of contamination. Calculated enrichment ratios ranged from relatively low 1.712 for Fe, 2.672 for Ni and 6.606 for Mn, through 90.657 for Cu up to to very high 628.056 for Zn and 767.875 for Pb and tremendously high 1017.023 for Cd.

After intensive analyzes of the results were constructed set of diagrams where the actual metal values were compared with certain standard values (Figure 3).

In general, after summarizing all the facts, which have resulted from this research we could say that, as a direct consequence of intensive mining in the Toranica Mine during the previous years, was caused serious disturbance of the natural metal balance in sediments.

Also, in samples taken from the area of consideration were determiend increased concentrations of metals no matter how high they were in comparison with maximal values allowed by standards. The highest concentrations of metals in sediments is highest in the area of the tailling dam (Figure 3). The deposition of metals in the taillings took place during the long period of time and is understandable why the metal concentrations in sediments are very high there.

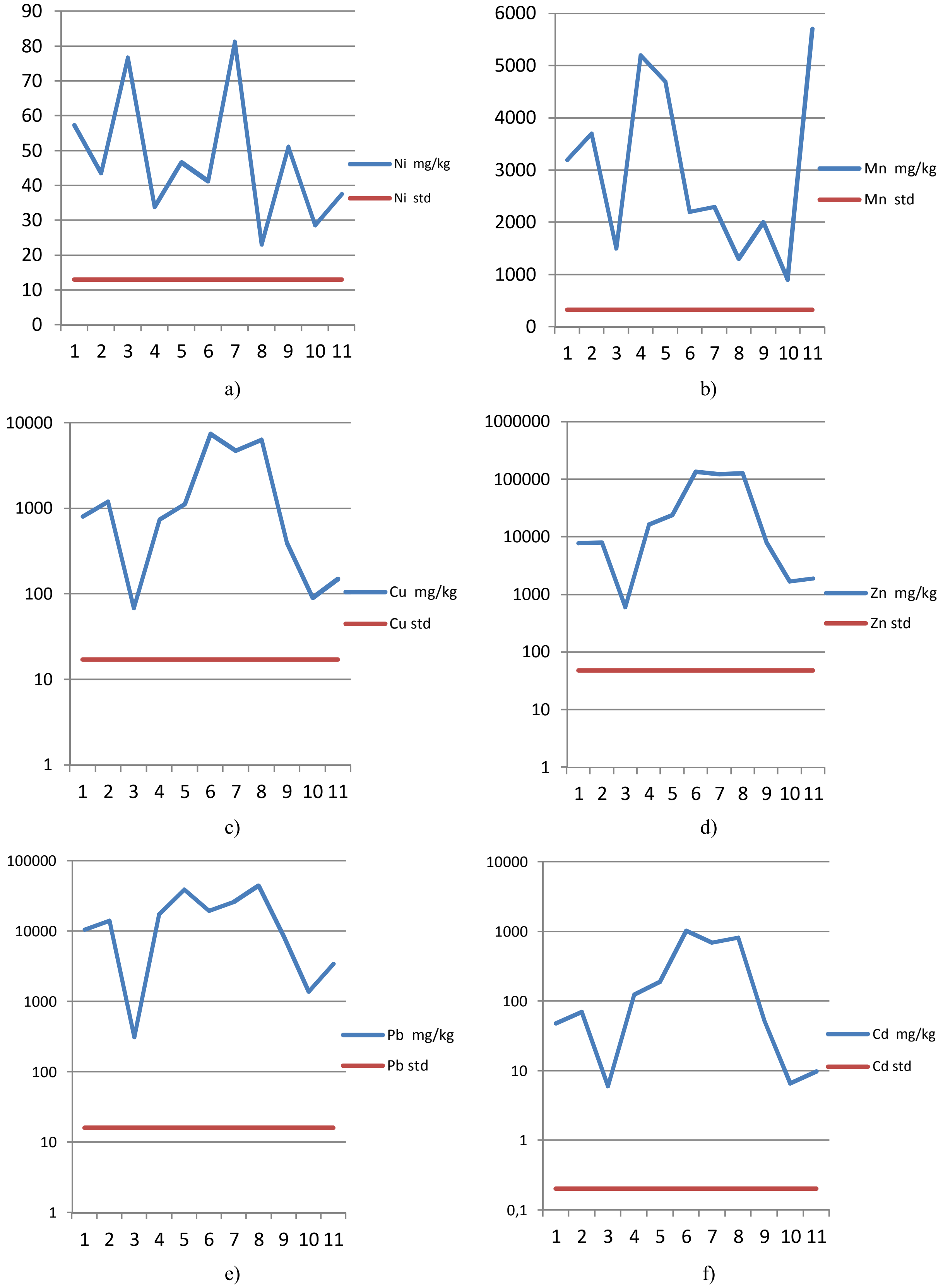


Fig. 3. Measured concentrations of some heavy metals vs. standard values in the adjacent vicinity of Toranica Mine near the city of KrivaPalanka, Macedonia
(*Note:* Plots *c, d, e* and *f* have logarithmic vertical scale)

However, detailed study of data determined trend that the concentrations decrease after the confluence with the river Kriva, but are still remain significantly elevated.

The Kocani basin

The Kocani basin trendsE-W and it is a typical symmetrical grabenbounded by normal faults on both its south and north sides. Basinal sedimentaryand volcanic rocks in the basin lie above metamorphicrocks of Precambrian age, sedimentary rocks of Eocene-Oligoceneage, and locally, igneous rocks of Oligocene–lower Miocene age.The sedimentary and volcanic rocks in the graben areincompletely exposed, but the lithostratigraphy of the section hasbeen well studied from several geothermal exploration boreholes,the deepest of which is 1100 m.The graben was initiated in middle Miocene time as a lacustrine basin that persisted until the late Miocenewhen lacustrine sedimentation was terminated by the influx of pyroclastic material, volcanic breccia, and lava flows. InPliocene time, a lacustrine environment was re-established and coarse-grained gravel and sandstone were deposited. Four formations can be distinguished, three of which are in superposition.

The *Zletovo Formation (ZlF)*is composed of ignimbrite, breccia, and lava flows of dacite, andesite, andlatite. These volcanic units created relief within the basin.

The *Usje Formation (UsF)*is not exposed but is known from several deep boreholes. It consists of 580 m of marl, marly claystone, claystone, sandstone, and siltstone that was deposited in one part of the graben simultaneously and interfingered with the volcanic rocks of the Zletovo Formation.

The *Probistip Formation (PrF)*in the Kocani graben is~280 m thick and consists of two lithological units.(*a*) The lower unit contains tuff and claystone. It is notexposed but is known from drill hole data and is up to 80 m thick.(*b*) The upper unit consists of up to 230 m of andesitic breccia and tuff with lava flows mostly of andesite, latite, and quartzlatite.

Rocks of the *Solnje Formation (SoF)*are exposed mostlyin the eastern parts of the basin where they are up to 100 mthick. The presence of a hiatus at the base of this formation is suspected. Intensive tectonic movements occurred during deposition of these strata lacustrine environments were reestablished (sandstone and gravel).

The *Quaternary sediments (Q)*are developed on the margins of the graben and represent alluvial-proluvial terraces.Locally, thin travertine layers occur in the southern partof the basin.

The anthropogenic influence to the Kocani soils was already confirmed in some former works such as those of Serafimovski et al., 2005; Rogan et al., 2005; Dolenec et al., 2005; Rogan et al., 2006; Dolenec et al., 2007.The objective of the latest study of the Kočani soil system area was evaluation of the environmental risk, in orderto determine the bioavailability of heavy metals in the soil samples, by the application of the sequential extraction method(leaching procedure). To evaluate the true short and longterm environmental impact of heavy metals in soils, already studied in Rogan et al.,(2009) and Rogan et al.,(2010), the most crucial factors to consider were their mobility and bioavailability through soil-plant systems. But only the soluble, exchangeable and chelated metal species in the soils are bioavailable in individual soil plant system (Kabata-Pendias & Pendias,2001). Therefore, assessing the environmental risks required the measurementof the total amount of heavy metals in soils and the total amount of heavy metals detected in the available fractions, also. The identification of heavy metals (Ag, As, Cd, Cu, Mo, Ni,Pb, Sb and Zn) mobility and availability in Kočani paddy soils was evaluated by sequential extraction procedure. A widely used modified method for the identification and evaluationof the availability or binding forms of heavy metals in soils is the sequential extraction procedure proposed by Tessier et al. (1979).According to the sum of the water soluble and exchangeable fractions for Ag, As, Cd,Cu, Mo, Ni, Pb, Sb and Zn measured in the paddy soils at KočaniField, the mobility and bioavailability potential of the heavy metals studied declined in the following order: Cd > Mo > Sb > Zn > Cu> As > Pb > Ni > Ag. Cd was consistently bound to bioavailable and leachable fractions, as were Mo and Sb, which were also significantly present in the oxidisable fraction (Figure 4).

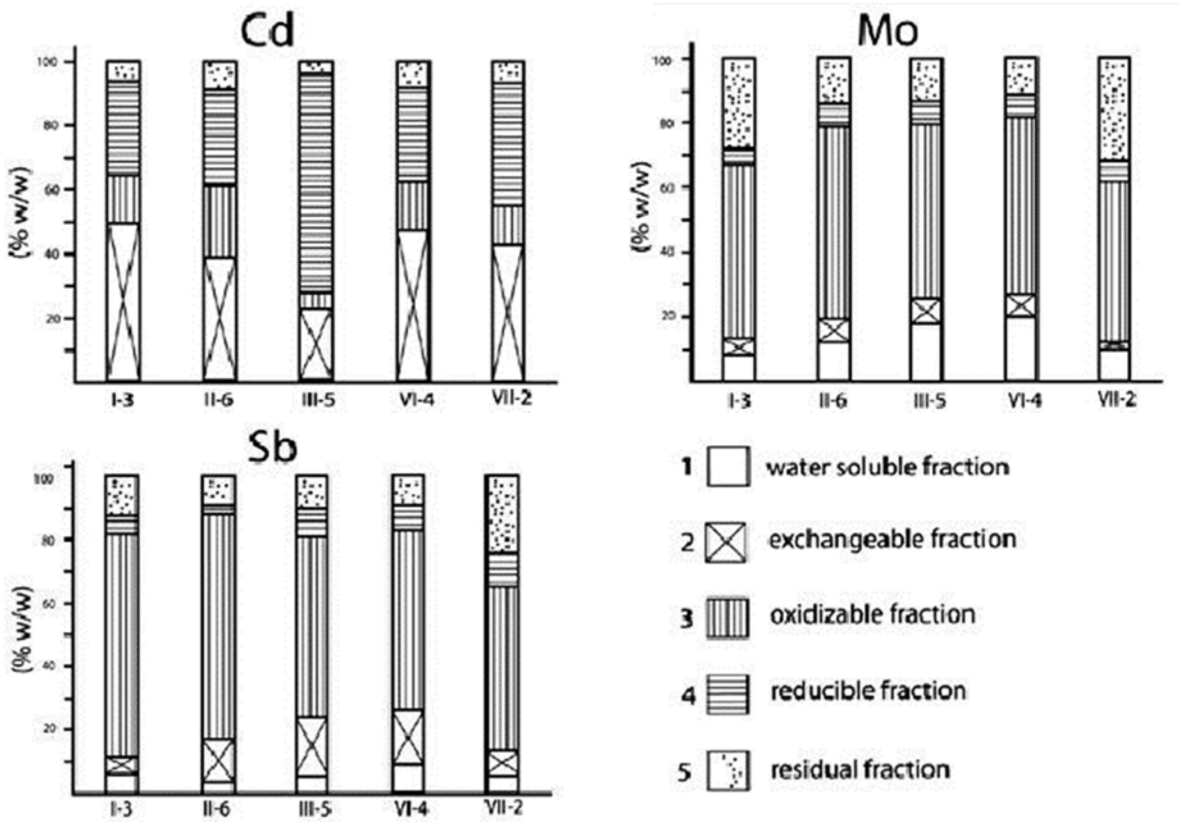


Fig. 4. Heavy metal binding forms in paddy soil samples from locations I-3, II-6, III-5, VI-4 and VII-2.

It is a must to mention that the increased cadmium concentrations are due to anthropogenic factors such as the use of phosphate fertilizers as well as the discharge of large concentrations of cadmium in the River Bregalnica as waste waters coming from the flotation plants of the Sasa and Zletovo Mines.Cu and As were mostly linked to the oxidisable fraction, indicating relative mobility under oxidising conditions. The reducible and reducible/residual fractions prevailed for Zn, Pb, Ni, and Ag, signifying a relatively low mobility capacity. Systematic study on heavy metal transfer from soils to crops, estimated daily intake for the local inhabitants of Kočani Field and project for diminishing heavy metal content in contaminated soils are essential.

The Lakavica basin

This basin that very specific in many ways is located in southeastern Macedonia and it is long and narrow (70 km long and 7 km wide) in its nature. This basin is partly developed above upper Eocene sediments. The graben formed during Pliocene time along reactivated older faults. The sedimentary section is ~300 mthick and is composed of the poorly exposed Vladevci Formation overlain by undifferentiated Quaternary sediments (Fig. 5).

The *Vladevci Formation (VlF)* consists of more than200 m of gravel and sandstone alternating with claystone andsandy claystone. To the east, the sedimentary graben fill overlaps the Bucim-Damjan-BorovDol volcanic complex. The sediments contain detritus of quartz, gneiss, granite, andesite, latite, andquartz-latite.

In some parts of the graben the *Quaternary sediments (Q)*are 100 m thick and consist of poorly sorted and poorly stratified gravel containing clasts of quartz, gneiss, granite, carbonates, and volcanic rocks.

The main anthropogenic input within this basin comes from the Buchim copper mine. The Buchim Mine is located in eastern central Macedonia, 10 km west of the town of Radovis. The Buchim's open pit mine has been in operation for 31 years and produced more than 500,000 t of ore annually and currently there are more than 120 Mt of ore reserves. The deposit is a porphyry copper type deposit with some small ore veins of lead-zinc mineralization where galena predominantly is concentrated in the marginal areas of the ore field(Serafimovski et al. 1996). The mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites. The ore consists of 0.3% Cu, 0.3 g/t Au, 1 g/t Ag, 13 g/t Mo, and 1- 4% pyrite; the igneous rocks have been altered to clays and micas.

The important metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite. Ore was concentrated by flotation on site and tailings were disposed to a dam in an adjacent valley. The main drainage system of the area consists of Topolnicka and Madenska River. The drainage area covers the mine and the ore processing facilities. All drainage occurs by gravity across the site. These rivers drains the S-SE and S-SW part of the mining area (around 150 km^2) and its contamination by heavy metals was expected to be increased.

The soil sampling programme complemented some of the previous programmes performed on watercourses and sediments of the Topolnicka and Madenska River that already have shown significant anthropogenic impact to the environment. The soil sampling was performed in the vicinity of Topolnicka and Madenska River enclosed in the famous Lakavica basin. The sampling programme was realized along profiles that were established perpendicular to the watercourse. Soil samples were taken perpendicular to the watercourse with 25 meters distance between each sample.The concentrations of these particular elements were in the range as follows: 8.57÷151.73 $mg \cdot kg^{-1}$ Pb, 40.64÷261.40 $mg \cdot kg^{-1}$ Zn, 3.15÷7.08 $mg \cdot kg^{-1}$ Cd, 35÷295.34$mg \cdot kg^{-1}$ Cu, 15.28÷360.42 $mg \cdot kg^{-1}$ Ni, 300÷1800 $mg \cdot kg^{-1}$Mn and 2.43÷5.26 % Fe. All of them were significantly above the NOAA reference values (Figure 5). Also, the calculated enrichment ratio (measured values over the reference value) speaks itself regarding the level of contamination. Namely, the enrichment ratios ranged from relatively low 1.724 for Zn, 2.07 for Fe and 2.372 for Mn and 2.866 for Pb, through the medium 25.237 for Cd and 35.229 for Cu. These results and findings perfectly matched those by other researchers (Alderton et al., 2005; Serafimovski et al., 2005).

Beside the usual heavy metals suite were analyzed few other metals such as: Al, Sr, Ba, Cr, Co, V, As and Ag. For most of them, with an exception for Sr, were determined significantly increased values regarding the standards. All the elements were closely related to the mineral assemblage within the deposit or the ore treatment in the technological process (such is a case with Ba) so that their higher levels are direct consequence of the mine production.

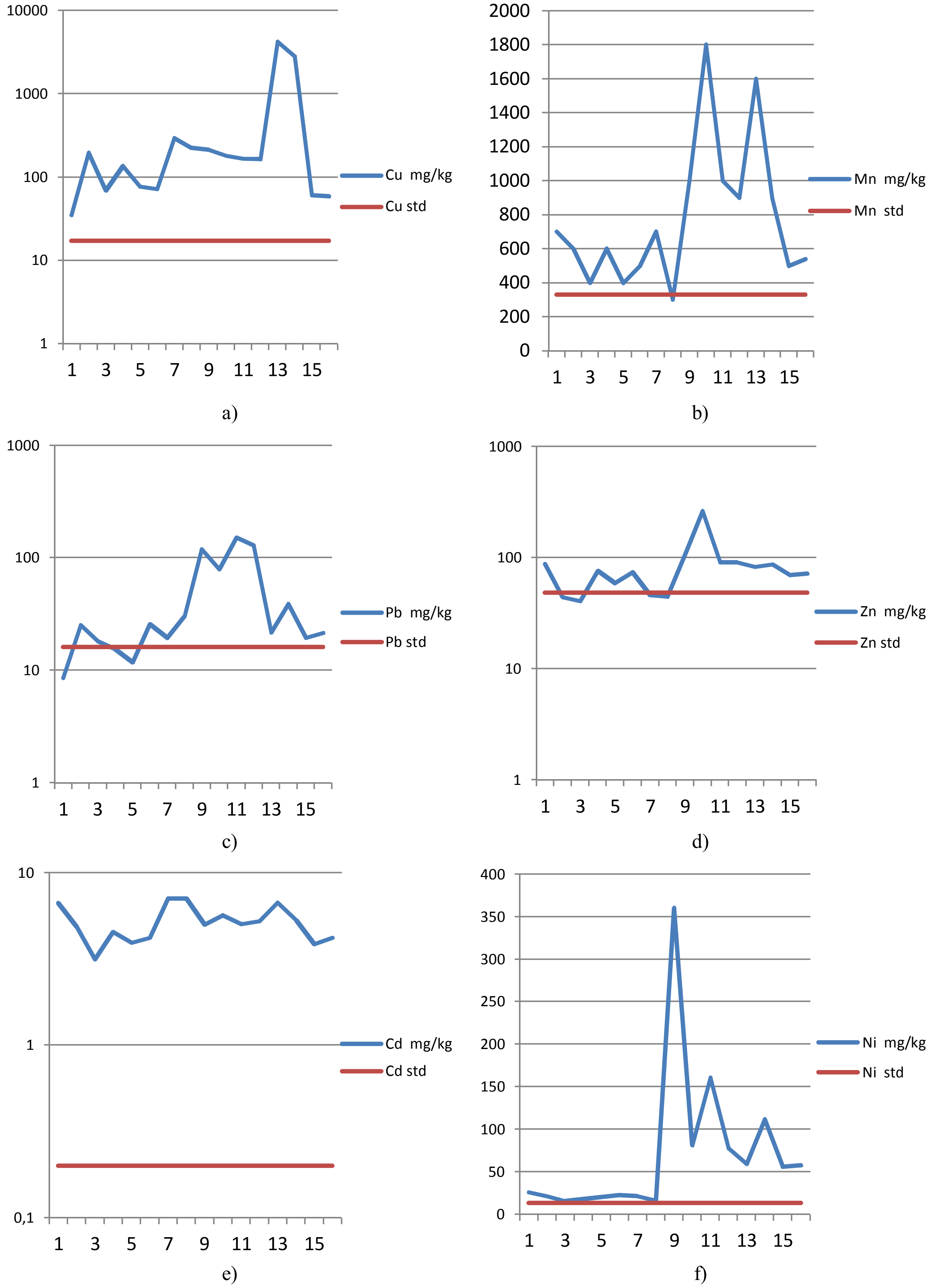


Fig. 5. Measured concentrations of heavy metals vs. standard values in soils taken perpendicular to the Topolnica and Madenska River in the vicinity of the Buchim Mine, near the Radovis, Macedonia (*Note:* Plots *a*, *c, d,* and *e* have logarithmic vertical scale)

As it was pointed above, the main reasons for increased pollution of soils in this area should be the geology and composition of rocks and mineralizations, organic fertilizers used on arable soils etc., (Younger, et al., 2002a, b). During the study were determined two major and one minor so called "hot spots". The major ones are the tailing dam near the Topolnica village while the other one is caused by drainage system from the Bucim Mine. The minor one has been located near the PilavTepe hill where has been detected influence from the former iron mine, Damjan.

After all, the results and conclusions that came out from this analysis of the close proximity of the Bucim Mine it remains the open question the bioavailability of determined metals and metaloids and possibility of their inclusion into the food chain.

The Veles basin

The **Veles basin (3)** has an irregular shape, but is generally elongated NE-SW. It has been determined from outcrop profiles and shallow boreholes, the thickness of the sedimentary section varies from300 to 350 m. The strata of the graben lie unconformably above Paleozoic metamorphic rocks, Triassic, Upper Cretaceous, and Upper Eocene sedimentary rocks and Jurassic ultrabasic rocks.

Sedimentation began in the Meotian, continued in the Pontian, and, following a clear hiatus between the Pontianand the Dacian stages, Pliocene sedimentary rocks wereextensively developed. In general it is composed of three formations.

The *Veles Formation (VeF)*that is composed of sandstone, gravelly sandstone, claystone, andsandy claystone (200–250 m thick). In the upper part of the formation, layers of marly limestone 2.5 m thick occur. In the Ovce Pole part of the Veles graben at the village of Kisino, the Veles Formation is intruded by calc-alkaline basalt.

The *Solnje Formation (SoF)*is exposedin the western and northern part of the Veles basin, where it extends into the Skopje and Kumanovo basins. In the western part of the Veles basin, strata of these Pliocene sediments also lie above pre-Miocene rocks that suggest increased tectonic activity and enlargement of the basin to the west due to sedimentation. The formation consists of poorly stratified coarse gravel, sandstone and sandy claystones.

The *Quaternary sediments (Q)* are preserved in the western part of the Veles graben, particularly along the Babuna River where they consist of glacial fluvial gravel, transported by the glaciers from Jakupica Mountain (10–30 m thick). Alluvial-proluvial Quaternary sediments are developed along theVardar River.

Topilnica Veles (smelting plant Veles) was the largest capacity for lead and zinc in former Yugoslavia with the capacity for producing 65 000 tons of zinc and 35 000 tons of lead per year whereas the entire production was exported.

The anthoprogenic impact in that particular part of the Veles basin has been studied at two regions around the former Pb-Zn smelting plant near Veles, performed during the 2008. In fact the study was concentrated on two separate areas, one of them around the BashinoSelo, a village to the north of the smelting plant and area to south of the smelting plant located close to the city limits.

Within the first area were sampled two parallel profile lines and one profile line normal to them while at the second area were sampled only two parallel lines. The samples were taken at distances of 30 meters between each other (Figure 6).

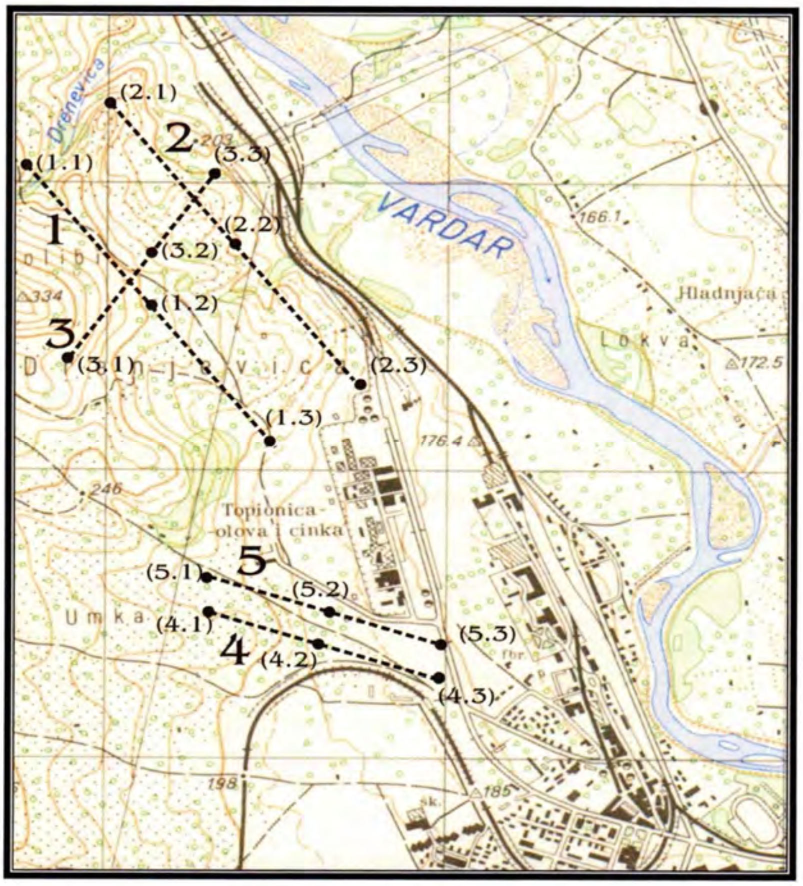


Fig. 6. Spatial distribution of profile lines and sampling points along them

The samples were analyzed to a standard array of elements: Pb, Zn, Cd, Cu, Ni, Fe and Mn, in general characterized as heavy metals.

The concentrations of these particular elements were in the range as follows: 20÷1823 $mg \cdot kg^{-1}$Pb, 29÷2395 $mg \cdot kg^{-1}$Zn, 28÷65 $mg \cdot kg^{-1}$Cd, 27÷81 $mg \cdot kg^{-1}$ Cu, 39÷164 $mg \cdot kg^{-1}$Ni, 508÷938 $mg \cdot kg^{-1}$Mn and 1.6÷3.8% Fe. All of them were significantly above the NOAA reference values. Also, the calculated enrichment ratio (measured values over the reference value) speaks itself regarding the level of contamination. Namely, the enrichment ratios ranged from relatively low 1.67 for Fe, 2.41 for Mn and 3.27 for Cu, through the medium 8.33 for Ni and 29.95 for Zn up to high 64.05 for Pb and the highest 237.67 for Cd. These results and findings perfectly matched those by other researchers that very same year (Stafilov et al., 2008a).

The group that comprises of Cd, Pb and Zn, as chemical elements that have been introduced into the environment through the anthropogenic activities (Stafilov et al., 2010), have shown the highest values in sampled and analyzed soils around the Veles smelting plant. That was expected even at the beginning of the study, but tremendously high values exceeded expectations. These finding are given very illustratively on the plots at Figure 7.

Also, after detailed study it was determined that values from respective sampling points were spatially dependent.

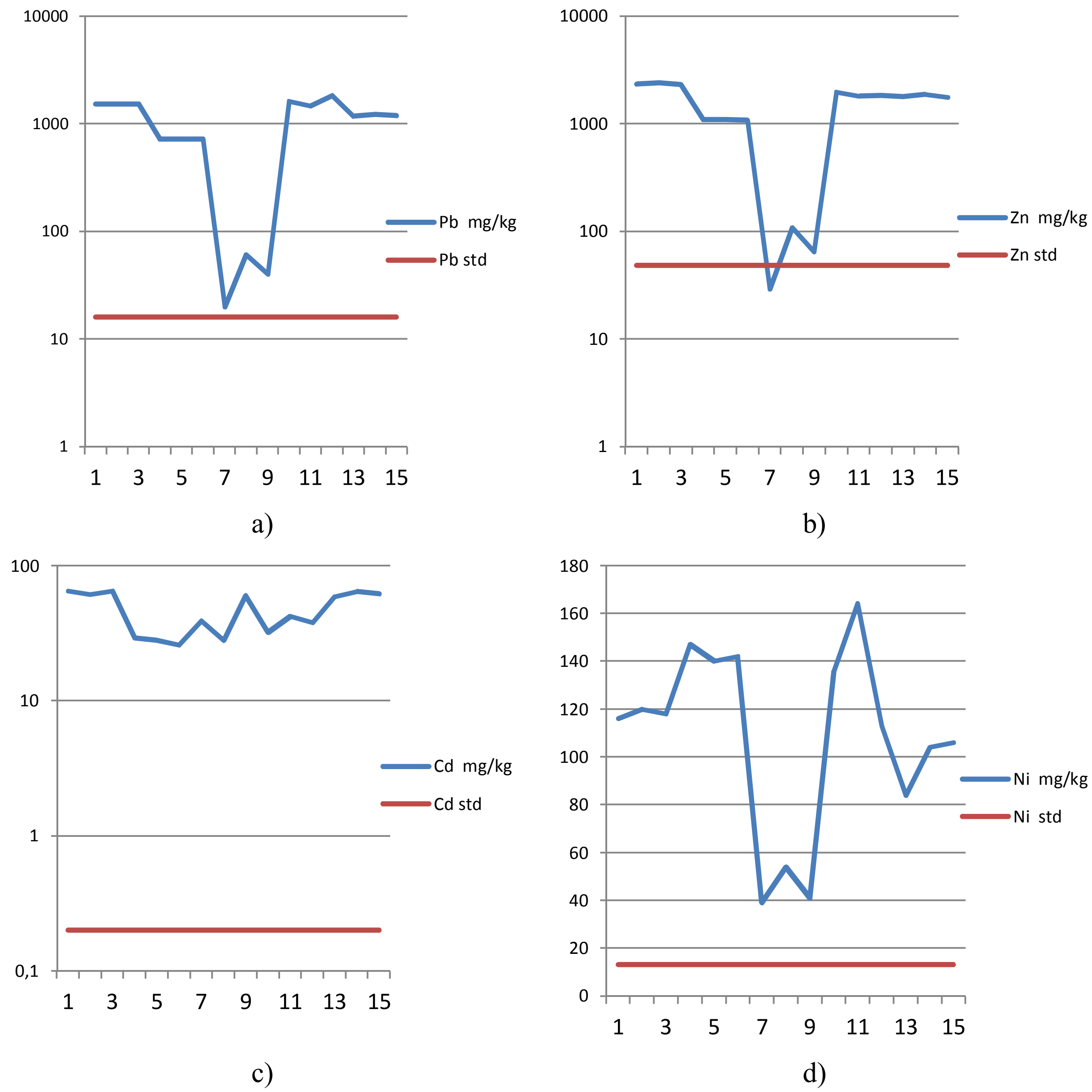


Fig. 7. Measured concentrations of some heavy metals vs. standard values around the former MHKZletovo's smelting plant near the city of Veles, Macedonia
(*Note:* Plots *a, b*and *c*have logarithmic vertical scale)

Namely, as can be seen from the diagram and sampling location map, the lowest values were determined at topographically higher places than those for lower ones. Ones again this makes clear the correlation between the pollution and smoke dust produced by the activity of former smelting plant in Veles.

The Tikveš basin

This is located in centralsouthern Macedonia and is developed above rocks of the Vardar zone or at their margins above the Pelagonian Massif. The northern part of the basin is elongated N-S and is bounded on its western side by normal faults of N-S and NW-SE strike (see map). The basin was connected with Central Macedonian Lake that extended across the Skopje, Kumanovo,Velesand Tikves basins. Strata in the Tikves basin mostly lie unconformably above Eocene flysch, but in the western and southern part of the basin they overlie Triassic, Jurassic, and Cretaceous sedimentary rocks and Jurassic ophiolites. During Late Pliocene time, the lake deposits of the basin were greatly enlarged and extended to the west into the Raec graben where the basinal strata consists of sandstone, gravel, and sandy clay-stone with travertine beds of Pliocene and Pleistocene age. Three formations are recognized in the central and southernpart of the Tikves basin.

The *Nerezi Formation (NeF)*is the oldest formation in the Tikves basin where sedimentation was continuous to the end of Miocene time. It is composed of three superposed lithological units that rest unconformably on Eocene sedimentary rocks.(*a*) The basal unit composed of basal conglomeratewith gravel, sandstone, and brown claystone(~l40 m thick) overlain by100 m of sandstone and mottled claystone. (*b*) The middle unit (~100 m thick) is mainly developed in the center of the basin where the basal strata are interbedded grey claystone, coal-bearing claystone and coal beds overlain by marl and marl-rich beds 40–50 m thick. (*c*) The upper unit occupies a large area of the basin and it consists of interbedded sandstone, siltstone, and silty claystone (120 m thick).

During the deposition of the *Vitacevo Formation (ViF),* tectonic activity increased, causing widening of the Tikves basin to the west and deposition of volcanic and volcanicla-sticrocks that cover a large part of the basin. The formation is 400 mthick and is best exposed in the area of Vitacevo. Basal beds, 100 m thick, consist of sandstone overlain by tuff and agglomerate with diatomite and tuff at the top. These beds are overlain by interbedded yellow sandstone, tuff, and agglomerate, locally containing travertine. One travertine bed is 15 m thick and extends laterally 40 m. The topmost part of the formation consists of ~100 m of agglomerate and tuff.

The *Mariovo Formation (MaF)*consists of strata deposited in a lacustrine environment that was terminated during Pleistocenetime by deposition thick beds of breccia conglomerate with volcanic material that reaches ~100 m thick in the western parts of the graben. Above these beds is 150 m of agglomerate, tuff, volcanic breccias, and locally travertine.

The supposed major source of anthropogenic environmental impact within this basin is the FENI Industries's smelting plant. The environmental concern has been intensified by the fact that the smelting facility is accommodated in the hearth of the well-known wine pro-ducing Tikveš region where remains of old civilizations point out to a wine producing even at 4th century BC. The FENI Industries's nickel ore, the one that goes into the smelting process, is a mixture of the lower grade ore from the Rzanovo Mine and ores imported from Indonesia, Philipines, Greece, Turkey and Albania.

In general the FENI Industries's plant is a two-line, rotary kiln electric furnace facility with the biggest rectangular electric furnaces of their kind in the world. The plant has been in operation since 1982 and produced approximately 5 000 t of nickel metal annually. Since it has been acquired by Cunico Resources in 2005 it steadily increased the production to 16 000 tonnes per year, while with planned refurbishments and improvements it will reach an annual production of up to 22 000 tons eventually.

Bearing in mind these facts we have proceeded with a soil sampling programme around the FENI Industries facility at two separate localities, one on the northwest of the smelting plant and the other one on the south-southeast in regards to the position of the smelting plant. In both cases the samples were sampled along two parallel profiles and one perpendicular to them (Figure 8).

The samples were analyzed to a standard array of elements: Pb, Zn, Cu, Ni, Fe, Cr, Co and Mn, in general characterized as heavy metals.

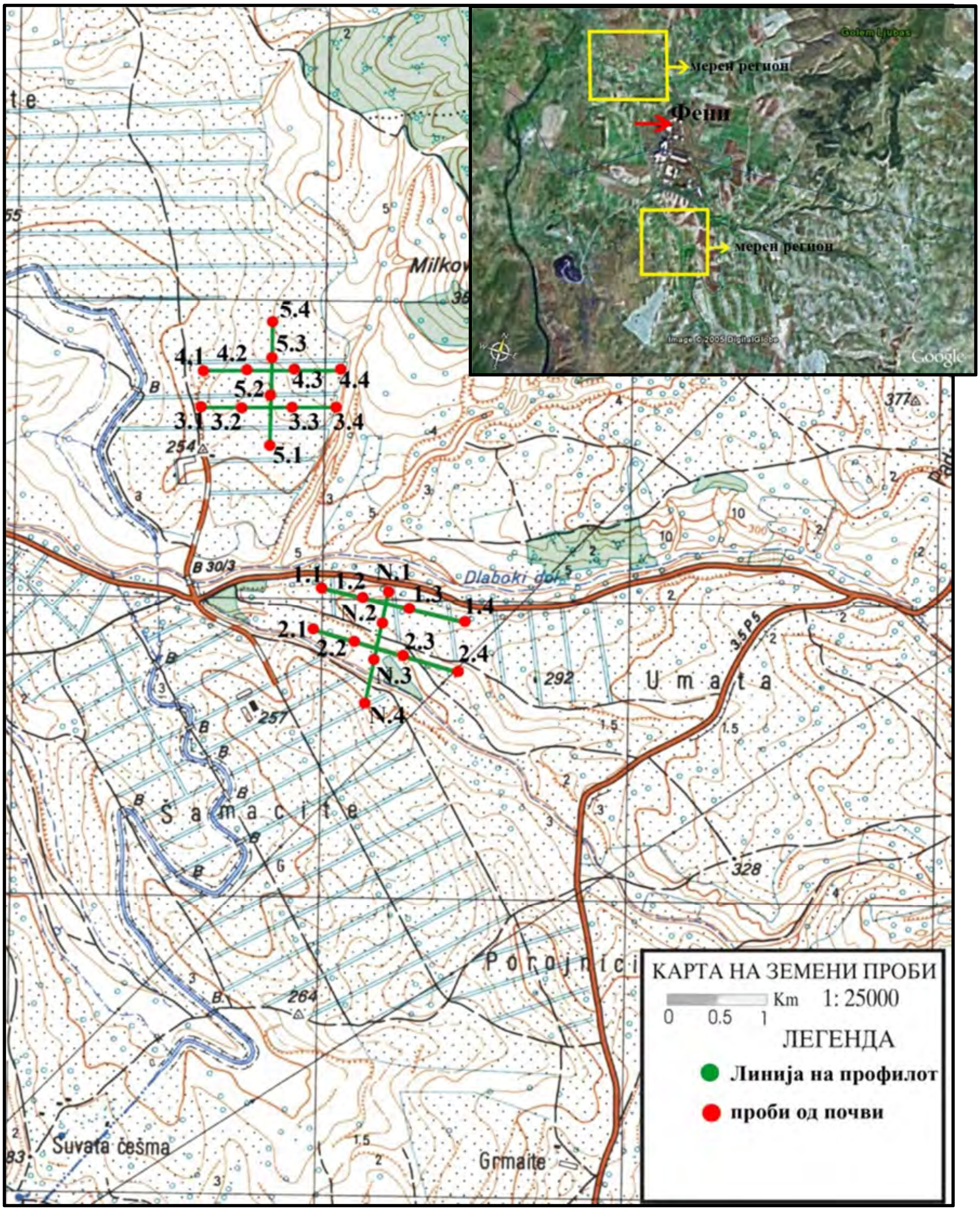


Fig. 8. Sampling locations around the FENI Industries smelting plant, small inset at the right upper corner gives the satellite position of the area.

The concentrations of these particular elements were in the range as follows: 16÷31 mg·kg^{-1}Pb, 117÷286 mg·kg^{-1}Zn, 13÷30 mg·kg^{-1}Co, 43÷119 mg·kg^{-1} Cu, 158÷292 mg·kg^{-1}Ni, 519÷903 mg·kg^{-1}Mn, 119÷236 mg·kg^{-1} Cr and 2.24÷3.79% Fe. All of them were significantly above the NOAA reference values. Also, the calculated enrichment ratio (measured values over the reference value) speaks itself regarding the level of contamination. Namely, the enrichment ratios ranged from relatively low 1.873 for Fe, 2.188 for Mn and 3.801 for Cu, through the medium 16.987 for Ni and 3.225 for Zn up to high 1.471 for Pb and the highest 2.823 for Co and 5.0124 for Cr.

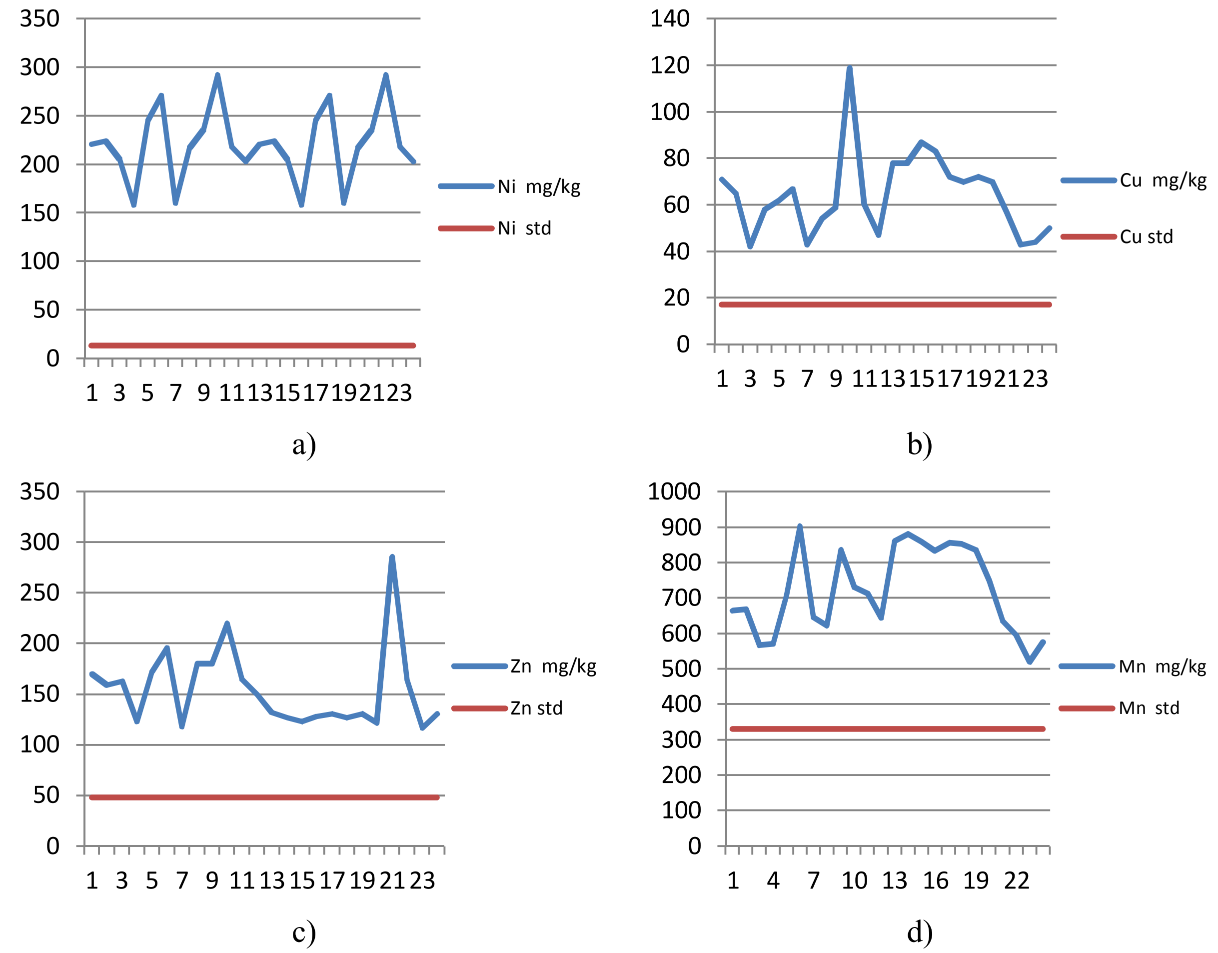


Fig. 9. Measured concentrations of some heavy metals vs. standard values around the Feniindustries's smelting plant near the city of Kavadarci, Macedonia

These concentrations are increased without any doubts, but bearing in mind the findings of Stafilov et al., (2008b, 2010), they probably cannot be attributed solely to the anthropogenic input. Namely, even background values of the heavy metals, especially of those for Ni, Cu, Co, Sb, Zn etc. It is probable that the FENI Industry plant, oposite to the obvious environmental impact has not contributed enormously to the measured heavy metals, since their background values were already at naturally higher levels. Our believes are that the situation will not change much since the current operator and owner the Cunico Resources is committed to upholding environmental laws, which dedication have resulted in a recent IPCC (Integrated Pollution Prevention and Control) permit that FENI Industries was granted on among the first in Macedonia.

Conclusion

Anthropogenic distribution considered as the pollution when chemical elements are introduced into the environment through human activities in the case of the treated basins have shown interesting. We have to point out that in all basins that were subjected to this study was determined significant environmental pollution that in general could be attributed to the anthropogenically induced processes and activities. Especially increased were concentrations of lead, zinc, copper, cadmium, manganese, molybdenum and other associated heavy metals. Their concentrations, all together with enrichment factors pointed to medium to strong anthropogenicaly introduced pollution.

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.

Dolenec, T., Dolenec, M., Serafimovski, T., Dobnikar, M., Tasev, G. and Pivko, B., 2005: Influence of mining related activity on heavy metals in water and sediment from the Kalimanci Lake (NE Macedonia). Mineral Deposit Research: Meeting the Global Challenge, *Ed.Jingwen Mao and Frank P. Bierlein*. 8th SGA Biennial Meeting,Beijing, China, pp. 840-845.

Dolenec, T., Serafimovski, T., Tasev, G., Dobnikar, M., Dolenec, M. and Rogan, N., 2007. Major and trace elements in paddy soil contaminated by Pb–Zn mining: a case study of Kocani Field, Macedonia. *Environ Geochem Health (207) 29, pp. 21-32*

Dumurdzanov, N., Serafimovski, T. and Burchfiel, B. C., 2005. Cenozoic tectonics of Macedonia and its relation to the South Balkan extensional regime. Geosphere August 2005 vol. 1 no. 1, pp. 1-22

Rogan Šmuc, N., Dolenec, T., Serafimovski, T., Tasev, G.andDolenec, M., 2010. Distribution and mobility ofheavy metals in paddy soils of theKočani Field in Macedonia. *Environmentalearthsciences*, 61, 899–907.

Rogan, N., Dolenec, T., Serafimovski, T., Dolenec, M., Tasev, G. and Dobnikar, M., 2005: Trace metal concentrations of water, paddy soil and rice of the Kočani Field (Eastern Macedonia) due to base metal mining activities. Mineral Deposit Research: Meeting the Global Challenge, *Ed.Jingwen Mao and Frank P. Bierlein*. 8th SGA Biennial Meeting, Beijing, China, pp. 837-840.

Rogan, N., Serafimovski, T., Dolenec, M., Tasev, G. and Dolenec, T., 2006: The distribution of rare earth elements (REEs) in paddy soil and rice seeds from Kocani Field (Eastern Macedonia). RMZ-Materials and Geoenvironment, Vol. 53, No. 4. pp. 433-444, Ljubljana-Slovenia.

Rogan, N., Serafimovski, T., Dolenec,M., Tasev, G.and Dolenec, T., 2009. Heavy metalcontamination of paddysoils and rice (*Oryza sativa* L.)from Kočani field (Macedonia). E*nvironmental Geochemistry andHealth*, 31, 439–451.

Serafimovski, T., Alderton, H. M. D., Dolenec, T., Tasev, G., and Dolenec. M., 2005:Heavy metals in sediments and soils around the Bucim copper mine area. *Geologica Macedonica,* Stip. Volume 19, pp. 69-81.

Serafimovski, T., Dolenec, T., Tasev G., and Dolenec, M., 2005: Metal Pollution of Soils in the SW part of Kocani Valley (R. Macedonia) Related With Pb-Zn Mines Activities. 5th International Scientific Conference "Modern Management of Mine Producing, Geology and Environmental Protection", Albena, Bulgaria. pp.249-256.

Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski, M., 2008b.Geochemical atlas of Kavadarci and the environs.Faculty of Natural Sciences and Mathematics-Skopje, University "Sts. Cyril and Methodius"-Skopje (ISBN 978-9989-668-74-6), 109 p.

Stafilov, T., Šajn, R., Boev, B., Cvetković, J., Mukaetov, D., Andreevski, M. and Lepitkova, S., 2010. Distribution of some elements in surface soil over the Kavadarci region, Republic of Macedonia.Environmental Earth Sciences, Volume 61, Number 7, pp. 1515-1530

Stafilov, T., Šajn, R., Pančevski, Z., Boev, B., Frontasyeva, V. M. and Strelkova, P. L., 2008a. Geochemical atlas of Veles and the environs.Faculty of Natural Sciences and Mathematics-Skopje, University "Sts. Cyril and Methodius"-Skopje (ISBN 978-9989-668-73-6), 123 p.

Younger, P.L (2002b). *Mine water pollution from Kernow to Kwazulu-Natal: geochemical remedial options and their selection in practice.* Geoscience in south-west England, 10, 255-266

Younger, P.L, Banwart, S.A and Hedin, R.S (2002a), *Mine Water: Hydrology, Pollution, Remediation*, Kluwer Academic Publishers, Dordrecht.

A SURVEY OF LEAD POLLUTION IN SURFACE SOILS IN MITROVICA REGION, KOSOVO

Milihate Aliu[1], Robert Šajn[2], Trajče Stafilov[3]

[1] *Faculty of Medicine, Prishtina University, Bulevardi i deshmoreve, Prishtina, 10000, Kosovo*
[2] *Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia*
[3] *Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162, 1001 Skopje, Republic of Macedonia*

Abstract: The results of study on the spatial distribution of lead in topsoil (0-5 cm) over the Mitrovica region, Kosovo, are reported. The investigated region (301.5 km^2) is covered by a sampling grid of 1.4×1.4 km. In total 159 natural surface soil samples (0-5 cm) from 149 locations were collected. All samples were analysed using inductively coupled plasma – mass spectrometry (ICP-MS). Data analysis and construction of the map were performed using the Statistica (ver. 9), AutoDesk Map (ver. 2008) and Surfer (ver. 9) software. The obtained results show that the average content of lead in the surface soil for the entire study area is 450 mg/kg (with a range of 34–35000 mg/kg) which exceeds the estimated European Pb average of surface soil by a factor of 20. Enormously high contents are found in several sampling sites in towns of Zvečan and its surroundings (from 3400 mg kg^{-1} to 34500 mg kg^{-1}) and Mitrovica (from 5000 mg kg^{-1} to 4900 mg kg^{-1}). The most of the investigated soil samples collected mostly around the industrial zone in Southern Mitrovica, the Trepča mines in Stari Trg and valley of the River Ibar, downstream from the Zvecan, have the content of Pb in range between 1000 mg kg^{-1} to 3000 mg kg^{-1}. The lowest contents were found in the urban zone of the town of Vučitrn. The critically polluted area according to the New Dutch standards (over 530 mg kg^{-1}) covers 113 km^2 with the average content of lead of 530 mg kg^{-1}.

Keywords: Lead, soil, Trepča mines, smelter, spatial distribution, pollution, Mitrovica, Republic of Kosovo

Introduction

The main ores of Pb are galena (PbS) and cerusite ($PbCO_3$), but also in ores anglesite ($PbSO_4$) and crocoite ($PbCrO_4$) (Filipović and Lipanović, 1995). Anthropogenic emission of Pb is much higher than natural whereas biggest part is from internal combustion engine, burning of ore that contain Pb, uses of different Pb material removing of waste materials, making of colours, uses of some insecticide and burning of fossil fuels (Greenwood, 1984). Use of Pb as a fuel additive, its concentration in last 80 to 100 years has increased in environment (Hill, 1992). Lead is a very toxic heavy metal. The toxicity of lead is probably related to its affinity for cell membranes and mitochondria. Symptomatic lead poisoning in childhood is characterized by abdominal pain, anorexia, anemia, etc. In adults, symptomatic lead poisoning is characterized by abdominal pain, headache, irritability, anemia, peripheral motor neuropathy, and deficits in short-term memory. Chronic lead exposure is associated with interstitial nephritis, tubular damage, hyperuremia and chronic renal failure. An additional issue for both children and adults is whether lead that has accumulated in bone can pose a threat later in life, particularly in increased bone resorption (Klassen, 1996).

The effect on the environment pollution of mines and mining industries in Mitrovica is difficult to ascertain as little data exist. The problems are wide from hazardous material to air, soil and water pollution. In particular sites associated to the Trepča Mining Complex are of major concern as they have a long history on environmental pollution. The amount of metal produced was 2,066,000 t Pb, 1,371,000 t Zn as well as Ag, Bi and Cd (Palariet, 2003; Frese et al., 2004). Only several reports have indicated that current levels of lead exposure are extremely high in the soil and in the air as well (di Lella et al., 2003; Jia et al., 2004; Borgna et al., 2009). The main objectives of the present investigation were to determine the content of lead, to establish its spatial distribution in soils from the broad are of Mitrovica (Fig. 1) and to assess the size of the area affected by the smelter plant situated nearby.

Material and methods

Study Area

The Mitrovica is a city located in the north of Kosovo (Fig. 1) approximately 40 km north of Prishtina (the capital of the Republic of Kosovo). The study area (301.5 km^2) is large (24 NNW-SSE km x 18 WWS-EEN km), which is limited by the coordinates (WGS 84) longitude 20.74528°-20.99235° (E) and latitude 42.78522°-42.99330° (N). About 40% of study area lies at an altitude between 480-600 m (S and SE), but only 5 % has an altitude over 1000 m, mainly in the NE of the investigated area. On the aforementioned plain are located all the major urban zones (Zvečan, Mitrovica and Vučitrn), but also the main industrial zones, particularly around Zvečan and Mitrovica (Aliu et al., 2010, 2010a; Stafilov et al., 2010).

Of the total 301.5 km^2 of the study area, the water surface (rivers and lakes) covers 1.6 km^2 or (0.6 %), open area mainly cultivable land 160 km^2 (53 %), non-cultivable area, mainly forests 117.5 km^2 (39 %), settlements 18.4 km^2 (6.1 %) and industrial area (industry zones, mines, quarries and tailings) 4 km^2 (1.3 %).

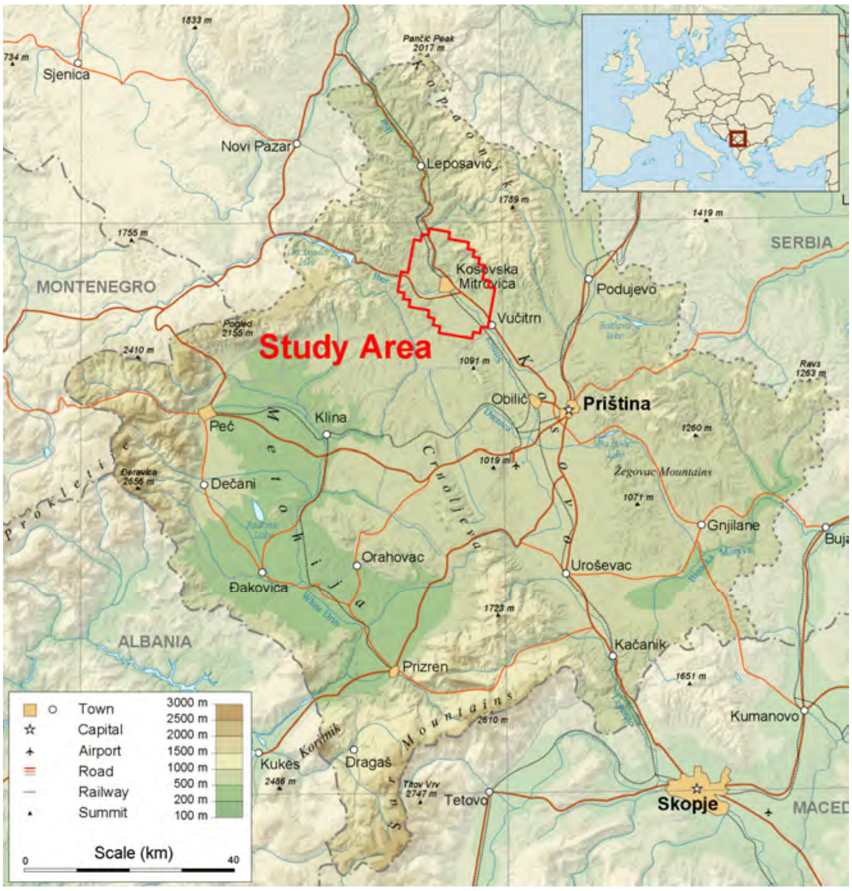


Fig. 1. Location of the study area

Sampling and chemical analysis

The sampling is done from January to May 2009. Surface soil samples (0 cm to 5 cm depth) were collected in the town of Mitrovica and surrounding region (Fig. 1). In total 159 samples were collected from 149 locations, including locations near mining centers of Mitrovica (Aliu, 2009, 2010; Stafilov, 2010). One sample represents the composite material collected at the central sample point itself and at least four points with the radius of 50 m around it towards N, E, S and W. The complete investigated region (301.5 km^2) was covered by a sampling grid of 1.4 x 1.4 km. Soil samples were air dried, crushed, cleaned from extraneous material and sieved through a plastic sieve with 2 mm mesh. The sieved mass was quartered and milled in agate mill. 0.5 g of each sample was used for digestion with HNO_3, HF, $HClO_4$ and HCl according to ISO 14869-1:2001(E) method. Lead was analyzed by using of atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian 715-ES).

Results and discussion

Clarke of Pb in soil amount to 35 mg/kg (Bowen, 1979). European average of Pb in topsoil is 23 mg kg^{-1} (XRF or mixed acid digestion) and 15 mg/kg after aqua regia digestion (Salminen, et al., 2005). Data from the descriptive statistics of measurements of Pb in topsoil from whole region are given in Table 1. As it can be seen, Pb average in soil for all study area is 450 mg kg^{-1} (median of 370 mg kg^{-1}) in range from 34 mg kg^{-1} to 35000 mg kg^{-1}.

Table 1. Descriptive statistics of measurements for lead in soil (values given in mg/kg)

N	*Dis.*	X, X_g	s, s_g	*Md*	P10	P90	Min	Max
156	Log	450	1141	370	110	2300	34	35000

N – number of observation; *Dis.* – distribution (Log – lognormal); *Md* – median; *X* – arithmetical mean, *X*g – geometrical mean; *s* – arithmetical standard deviation; s_g – geometric standard deviation; *Min* – minimum; *Max* – maximum; P_{10} – 10 percentile; P_{90} – 90 percentile.

Distribution of Pb average in surface soil according to the determined zone provides the highest concentrations are in the Zone I, extremely contaminated part of the study area (Table 2, Figs. 2 and 3). As it is expected the concentrations are decreasing from the Zone I to the Zone III. Enormously high concentrations are found in several following sampling sites in Zvečan and its surroundings (from 3400 mg kg^{-1} to 34500 mg kg^{-1}) and Mitrovica (from 5000 mg kg^{-1} to 4900 mg kg^{-1}). The dozen sampling sites have the concentrations of Pb in range between 1000 mg kg^{-1} to 3000 mg kg^{-1} mostly around the industrial zone (Pb smelter, battery and accumulator factory in Southern Mitrovica), the Trepča mines in Stari Trg and valley of the River Ibar, downstream from the Zvečan. The lowest concentrations were found in the urban zone of Vučitrn. In both, the determined zones and the main urban areas, the concentrations are very high according to the EU average for Pb in soil (Fig. 3).

Table 2. Average of the lead according to zones and urban area (in mg kg^{-1})

	Median EU	Study area	Zone (I)	Zone (II)	Zone (III)	Zvečan	Mitrovica	Vučitrn
N	-	156	30	65	61	5	11	8
Pb	23	450	2600	540	160	16000	1700	250

N – number of samples; Mean (EU) – European topsoil average (Salminen et al., 2005); Zone (I) – Extremely affected area with heavy metals (57 km^2); Zone (II) – Strongly affected area with heavy metals (117 km^2); Zone (III) – Relatively little affected area with heavy metals (128 km^2); Zvečan urban area; Mitrovica urban area; Vučitrn urban area

In the cross section of the profile A-B which showing distance from the point A to B in length of 26 km, it is possible to see change in concentrations (Fig. 4). The lowest concentrations are found in the SSE of the study (point B) around urban zone Vučitrn. The maximum values are again between Mitrovica and Zvečan, which decrease towards the point A. Even in the NNW part of the study are found samples with high concentrations of Pb.

Spatial distribution of Pb in surface soils of all study area is provided in the Fig. 5. The high content of this chemical element can be found in almost all study area, but the highest content is related for the the urban areas Mitrovica and Zvečan, the Trepča mine complex as well as for the alluvial plains of the river Ibar. Contamination expands to the north of the study area, towards the slopes of Mountain Kopaonik and to the NNE, towards the Rogozna Mountain.

The main source of Pb pollution is consequence of smelting activities in area of Zvečan. Pollution of study area with Pb is very strong. Concentrations of Pb exceed optimum (referent) value (The New Dutchlist) in approximately 287 km^2 and action value (The New Dutchlist) in 113 km^2 (Fig. 6). In general terms, these results obtained for Pb content in soils in Mitrovica and surrounding area (35,000 mg kg^{-1}) are in agreement with those obtained by Borgna et al., 2009 (37,123 mg/kg).

Fig. 2. Determinate polluted zones in the study area

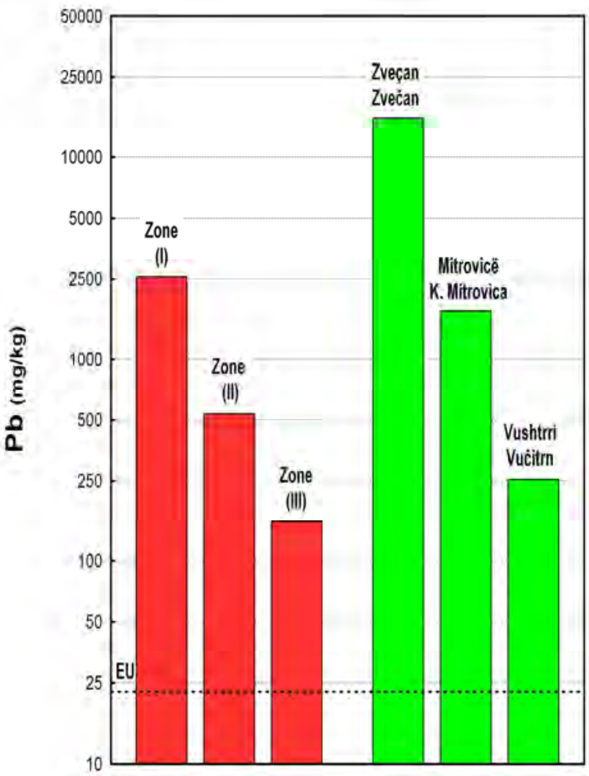


Fig. 3. Distribution of lead in topsoil according to zones and urban areas

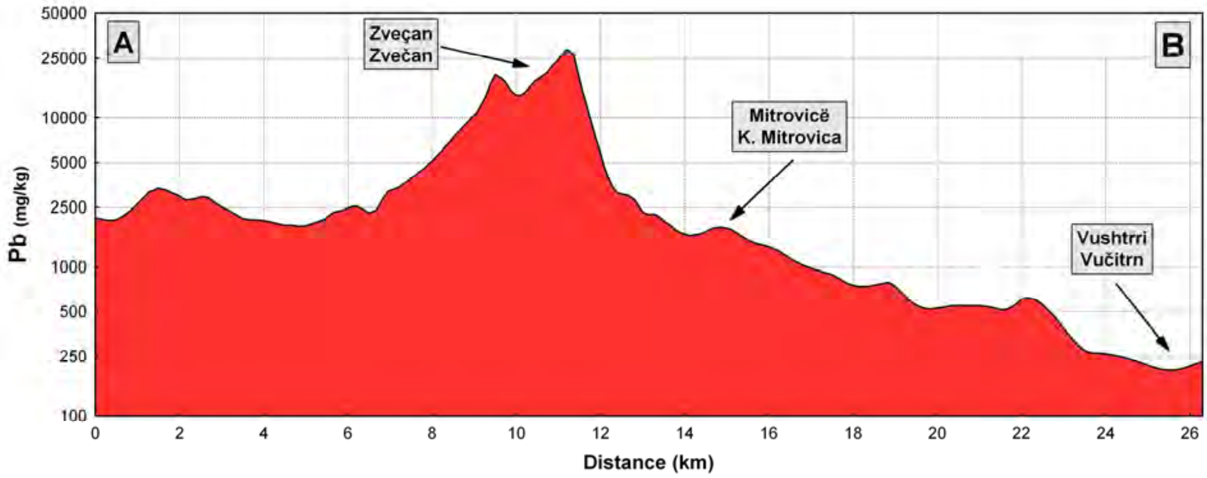


Fig. 4. Distribution of lead in topsoil (cross section - profile A-B)

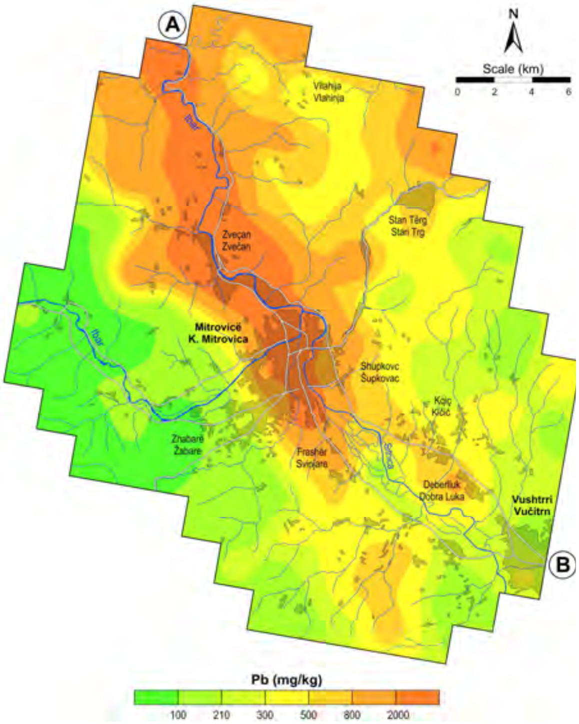


Fig. 5. Spatial distribution of lead in Mitrovica area

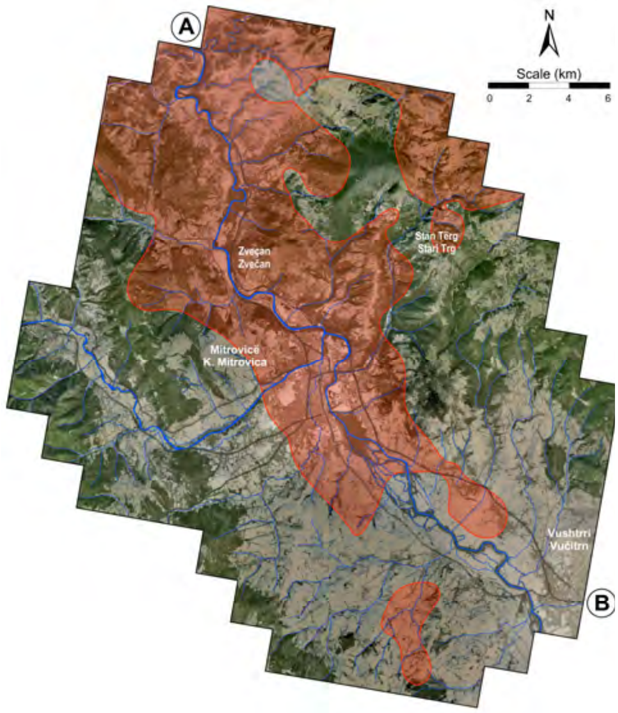


Fig. 6. Critically polluted area with lead in Mitrovica surface soil according to New Dutchlist

Conclusion

The results obtained in this study increase our knowledge of the Pb content in surface soils (0-5 cm) of the Mitrovica region, Kosovo. The Pb content in surface soils was found to range from 34 to 35,000 mg kg^{-1} with an average of 450 mg kg^{-1}. By comparing the obtained results with the data of the European lead average it appears that lead average in soils of Mitrovica region exceeds European lead average by a factor of 20. The highest Pb content was related to industrial zones and can be associated to the presence of anthropogenic sourses. In the region of Zvečan and Mitrovica several soil samples with extremely high content of lead are present. The spatial distribution of lead content in surface soils of Mitrovica region shows a extremely polluted area of 113 km^2 with the Pb average of 891 mg kg^{-1} (from 530 to 35,000 mg kg^{-1}). Therefore, it may be concluded that there is significant degree of lead pollution in the examined soils. Due to the extremely high Pb content found in soils, lead present a serious ecological and health risk in this site must be considered.

References

Aliu, M., Šajn, R., Stafilov, T. (2010). Distribution of cadmium in surface soils in K. Mitrovica Region, Kosovo, *Geologica Macedonica*, **23**, 27–34.

Aliu, M., Šajn, R., Stafilov, T. (2010a). Distribution of zinc in surface soils in K. Mitrovica Region, Kosovo, *Int. J. Pure Appl. Chem.*, **5**(4), 351-357.

Borgna, L., Di Lella, L.A., Nannoni, F., Pisani, A., Pizzetti, E., Protano, G., Riccobono, F., Rossi, S. (2009). The high contents of lead in soils of northern Kosovo. *J. Geochem. Explor*. **101**, 137-146.

Bowen, H.J.M. 1979: Environmental chemistry of the elements, Academic Press, New York.

Di Lella, L.A., Frati, L., Loppi, S., Protano, G., Riccobono, F. (2003). Lichens as biomonitors of uranium and other trace elements in an area of Kosovo heavily shelled with depleted uranium rounds. *Atmos. Environ*. **37**, 5445-5449.

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.

Filipoviović I., Lipanović S. (1995). Opća i anorganska kemija. Školska knjiga, Zagreb, p. 1145.

Frese, S.D., Klitgaard, R., Pedersen, E.K., Rank, J., Klemmensen, B. (2004). *Environmental Management in Kosovo, Heavy Metal Emission from Trepca*. II DM-2003/2004, Institut for Miljø, Teknologi og Samfund, Roskilde University, Roskilde.

Greenwood, N. N. (1984). Chemistry of the elements. Butterworth-Heinemann, Oxford, 1542 p.

Hill S.J. (1992). Lead. In: Stoeppler, M. (ed.): Hazardous metal in the environment, 231-255, Elsevier, Amsterdam.

Jia, G., Belli, M., Sansone, U., Rosamilia, S., Gaudino, S. (2004). Concentration, distribution and characteristics of depleted uranium (DU) in the Kosovo ecosystem: A comparison with the uranium behavior in the environment uncontaminated by DU, *J. Radioanal. Nucl. Chem*. **260**, 481-494.

Klassen, K. D. (Ed.), Casarrett and Doull's Toxicology, *The Basic Science of Poisons*, 5th ed., M. O. Amdur, J. Doull, eds. emeriti, McGraw-Hill, Health Professions Division, New York, 1996.

Palariet, M. (2003). *Kosovo's Industrial Giant, Trepca, 1965-2000*. European Stability Initiatives, University of Edinburgh, Edinburgh, U.K.

T. Stafilov, M. Aliu, R. Šajn, Arsenic in surface soils affected by mining and metallurgical processing in K. Mitrovica Region, Kosovo, *Int. J. Environ. Res. Pub. Health*, **7**, 4050-4061.

MONITORING DEPOSITION OF ANTHROPOGENIC INTRODUCED ELEMENTS IN AIR. CASE STUDY: COPPER MINE ENVIRON

Biljana Balabanova[1], Trajče Stafilov[2], Robert Šajn[3], Katerina Bačeva[2]

[1]Faculty of Agriculture, Goce Delčev University, Štip, Macedonia
[2]Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, POB 162, Skopje, Macedonia
[3]Geological Survey of Slovenia, Dimičeva 14, Ljubljana, Slovenia

Abstract

The total deposited dust was used as sampling media for monitoring the distribution of heavy metals in an area with intensively exploited copper minerals (Bučim copper mine, R. Macedonia). The content of Cu and Pb was determinate using atomic emission spectrometry with inductively coupled plasma (ICP-AES). Within the study area, three sampling spots (settlements) were selected: villages Bučim and Topolnica and the town of Radoviš. In the copper mine environ, there are some values above the national maximum permitted value for deposited dust (300 mg m^{-2} d^{-1}). Larger amounts of dust are deposited in the villages Bučim and Topolnica (annual average values of 489 mg m^{-2} d^{-1}, and 309 mg m^{-2} d^{-1} respectively) with a maximum value (815 mg m^{-2} d^{-1}) obtained in the Bučim village. Higher contents of Cu and Pb were obtained from deposited dust samples collected from Topolnica village (max. value 1183 mg kg^{-1} and 184 mg kg^{-1}, respectively).). In the town of Radoviš deposited dust was not above the maximum permitted amount for deposited dust, but higher content of Cu and Pb contents were found (max. values 1171 mg kg^{-1} and 189 mg kg^{-1} respectively).

Keywords: Total deposited dust, monitoring, heavy metals, copper mine, Republic of Macedonia

Introduction

Heavy metals in the atmosphere originated mainly from dust dispersion from metal refining, fossil fuel combustion, vehicle exhausts, and other human activities and stay in the atmosphere until they are removed by a variety of cleansing processes (Vallero, 2008; Agarval, 2009). Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust. Copper mine with open ore pit type present a potentially emission source of heavy metals in air. Main processes that allow it are: minerals blasting, drilling and crushing, their loading and transportation to processing and flotation plants. From other hand, large amounts of ore waste and flotation tailings are deposited at open, continuously exposited to air flow and winds caring-out. People are directly exposed to the effects of heavy metals through inhalation of airborne micro particles from atmospheric dust (Jarup, 2003; Godish, 2004).

Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic elements introduced into the atmosphere (Čačković et al., 2009). Fine powder with a high content of heavy metals is generated as a result of emissions from the processing of ores and metallurgical process and is distributed as a result of wearing the wind. Many investigations have focused on the chemical composition and the content of toxic substances in deposited dust (Morselli et al., 2003; Avila and Rodrigo, 2004; Polkowska et al., 2005; Vike, 2005, Stafilov et al., 2011).

In order to determine the amount of fine dust contained in the air, samples of total deposited matter (deposited dust) were collected at three locations in the area of Bučim copper mine, R. Macedonia.

Study area

The study area occupies the "Bučim" mine environ, located in the eastern Republic of Macedonia part (Fig. 1). The mine and the ore processing plant have been functioning since 1979 and it is assumed that the mine has about 40 million tons of ore reserves. Ore tailings are dropped out at open site near the mine, occupies a surface of 0.80 km^2. The ore tailings deposit has about 130 million tons of ore tailings. Exposure of this great mass of ore tailings to constant air flow and wind leads to the distribution of fine dust in the air.

Geological description. The Bučim-Damjan-Borov Dol area is divided into two tectonic blocks. The Bučim tectonic block and the southern tectonic block Damjan are a part of the Vardar zone. The blocks are divided by a fault of first order in the SE direction. Despite the disposition in two different tectonic blocks, the metallogenic area is unified based on the similarities of Tertiary magmatism and the analogous ore mineralisations. The Bučim copper-porphyry deposit with additional gold mineralisation is found in the northern block (Stefanova et al., 2004).

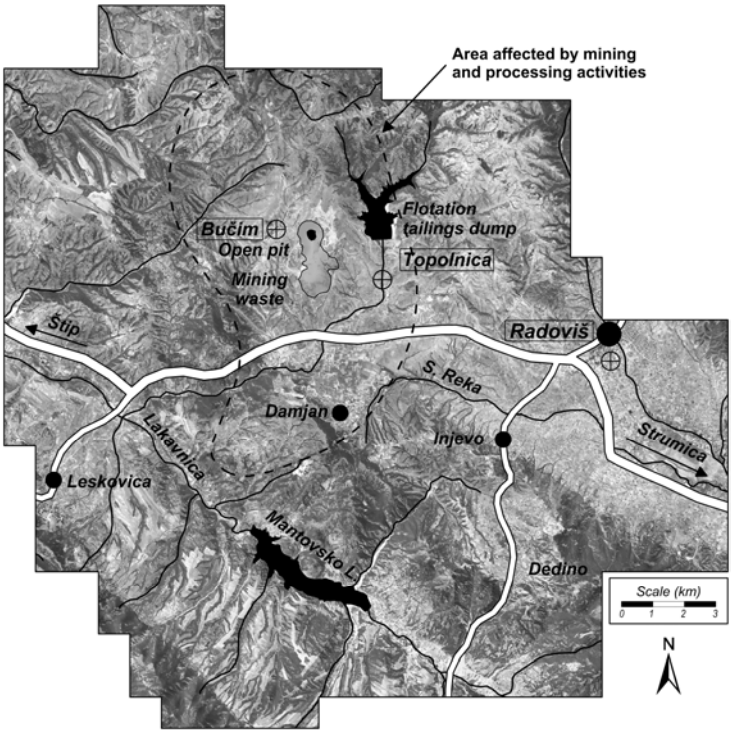


Fig. 1. Location of study area and sampling points for deposited dust

Experimental

Monthly samples of deposited dust were collected at three monitoring sites in copper mine environ: the town of Radoviš and the villages Bučim and Topolnica during 2009 (Fig. 1). Samples were collected using the dust deposition gauges. The obtained results were expressed in mg m^{-2} d^{-1} (i.e. the mass of dust deposited per m^2 per day). A deposit gauge, which comprises a 28±1 cm diameter funnel inserted into a plastic container (at least 5-10 liters in size) through a rubber stopper. Stand approximately 2 m tall and a canister which holds the plastic container to protect it from sunlight. After 30±2 days, any deposited matter in the funnel was washed into the plastic container using distilled water.

The collected rainwater of each sample was evaporated near dryness and then 3-5 mL of nitric acid, *p.a.* (MERCK, Germany) was added and transfers in to the 25 mL volumetric flasks. The content of Cu and Pb in digested samples was determined using ICP-AES (Varian 715-ES). The optimal instrumental parameters for this technique were previously given (Stafilov et al., 2011).

Results and discussion

The obtained values for the contents of the investigated elements were statistically processed using basic descriptive statistics. From the results obtained in this investigation it is evident that a large amounts of deposited dust were recorded in the close vicinity of the mine (villages Bučim and Topolnica) in some periods of the year the values are above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}). Maximum value for the total deposited dust (815 mg m^{-2} d^{-1}) was obtained in August in the Bučim village. The annual average for the total deposited dust in the vicinity of the Bučim village is 489 mg m^{-2} d^{-1}, for Topolnica the 309 mg m^{-2} d^{-1} and accounted for Radoviš is 97 mg m^{-2} d^{-1} (Fig. 2).

As it can be seen from the data presented in Table 1, 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 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 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) as presented in Fig. 3.

Table 1. Statistical parameters for annual values for the content of copper and lead in samples of deposited dust (in mg kg^{-1})

Element	N	Sampling site: Vill. Bučim		Vill. Topolnica		Radoviš	
		Median	Range	Median	Range	Median	Range
Cu	12	145	85.3-317	150	52.5-1183	396	94.8-1171
Pb	12	25.7	12.1-56.6	26.8	7.20-184	69.5	20.1-189

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; 2011; 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 (Fig. 4).

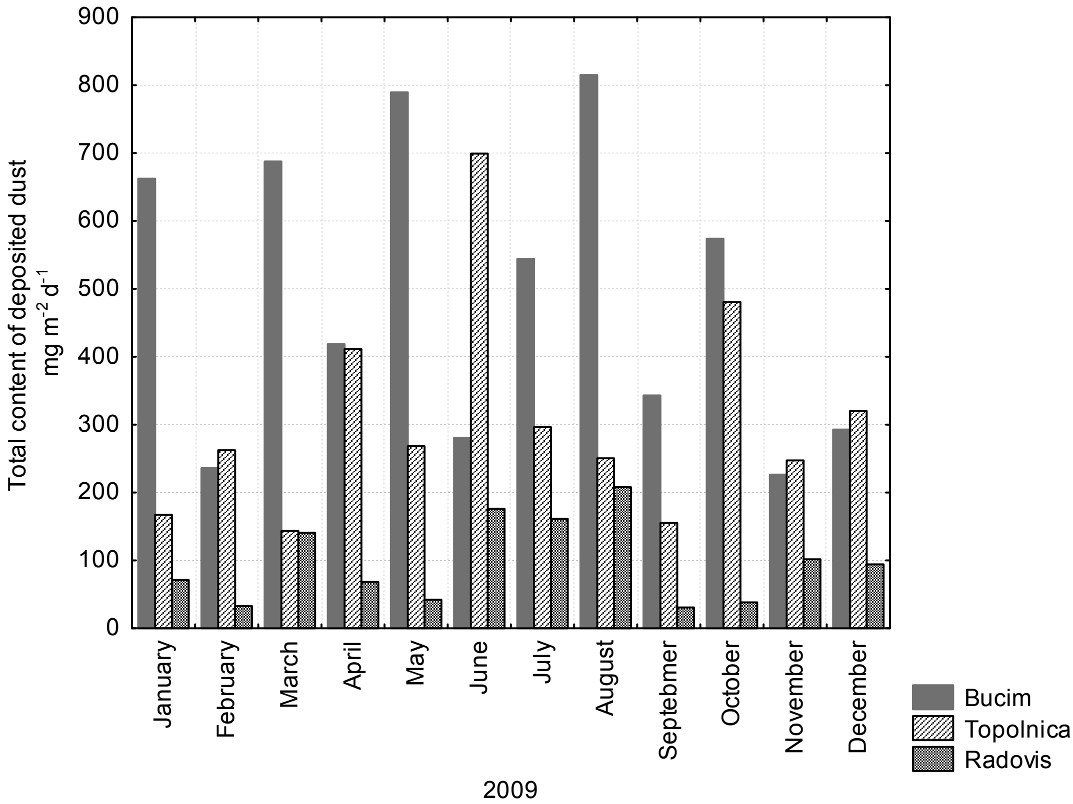


Fig. 2. The total content of deposited dust

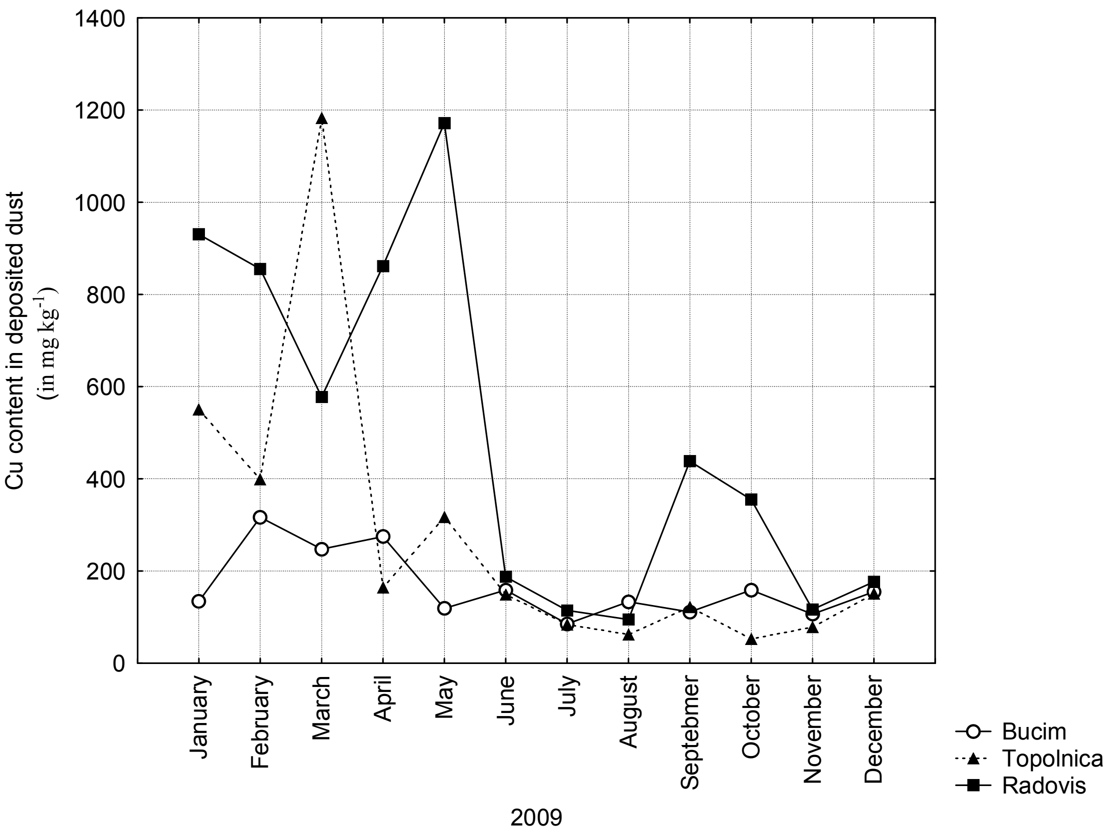


Fig. 3. Trends of copper content in deposited dust through the whole year

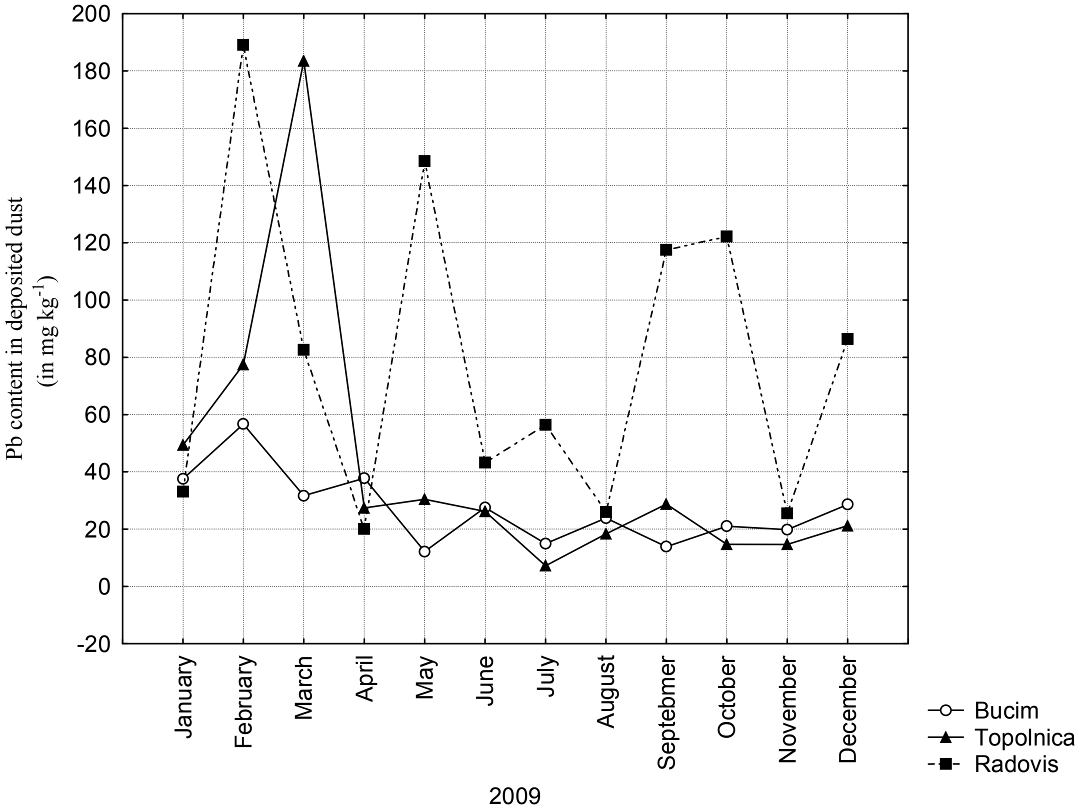


Fig. 4. Trends of lead content in deposited dust through the whole year

Conclusion

Conducted monitoring with deposited dust samples fortify that anthropogenic introduced elements (Cu and Pb) deposit in higher contents in close vicinity of their hot spots (open ore pit, ore waste and flotation tailings landfill). In the copper mine environ, there are some values above the national maximum permitted amount of sedimental dust (300 mg m^{-2} d^{-1}); annual average for the total deposited dust in the vicinity of the Bučim village - 489 mg m^{-2} d^{-1}, for Topolnica - 309 mg m^{-2} d^{-1} and for Radoviš - 97 mg m^{-2} d^{-1}. Maximum value for the Cu content was obtained from Topolnica village (settlement near by the flotation tailings landfill). In the town of Radoviš deposited dust was not above the maximum permitted amount for dust powder, but higher contents of Cu and Pb were obtained (with monthly variations in results). The high contents of Cu and Pb are not only due to mining works, but also the town works, traffic, industry and developed technological processes which aloud emission of higher amounts of these heavy metals in air.

References

Agarval, S. K. (2009). *Heavy metal pollution*. New Delhi, SB: A P H Publishing Corporation: Nangia.

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

Macedonia, *Journal of Environmental Science and Health, Part A, Toxic/Hazardous Substance & Environmental Engineering*, **45**, 1504–1518.

Balabanova, B., Stafilov, T., Šajn, R., Bačeva, K. (2011). Characterisation of heavy metals in lichen species *Hypogymnia Physodes* and *Evernia Prunastri* due to biomonitoring of air pollution in the vicinity of copper mine, *International Journal of Environmental Research*, (2011), in press.

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 and Toxicology*, **61**, 173–184

Čačković, M. Kalinić, N. and Vadjić, V. G. (2009). Pehnec heavy metals and acidic components in total deposited matter in Šibenik and National park Kornati, Croatia, *Archives of Environmental Contamination and Toxicology*, **56**, 12–20.

Godish, T. (2004). *Air quality.* 4th edition. Boca Raton, Lewis publishers.

Jarup, L. (2003). Hazards of heavy metal contamination, *British Medical Bulletin,* **68**, 167-182.

Lazarevski, A. (1993). *Climate in Macedonia*, Kultura, Skopje (in Macedonian).

Morselli, L. Olivieri, P. Brusori, B. and Passarini, F. (2003). Soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions in Bologna, Italy, *Environmental Pollution*, **124**, 457–469.

Polkowska, Z., Astel, A., Walna, B., Małek, S., Mędrzycka, K., Górecki, T., Siepak, J. Namieśnik, J. (2005). Chemometric analysis of rain water and throughfall at several sites in Poland, *Atmospheric Environment*, **39**, 837–855.

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

Stafilov, T., Šajn, R., Balabanova, B., Bačeva, K. (2011). Distribution of heavy metals in attic dust and deposited dust in the vicinity of copper ore processing and ferronickel smelter plants in the Republic of Macedonia, in: *Dust: Sources, Environmental Concerns and Control***,** Nova Science Publishers, Inc.**,** Hauppauge, NY, in press.

Stefanova, V. Neviealkov, R., Moritz, R. (2004). *Magmatism of the Borov Dol copper occurrence*, In Kovachev, V. editor. Proceedings on the Annual Scientific Conference of the Bulgarian Geological Society. Sofia, House of Science and Technology.

Vallero, D. (2008). *Fundamentals of air pollution.* 4th edition, Amsterdam, Academic Press Elsevier.

Vike, E. (2005). Uptake deposition and wash off fluoride and aluminum plant foliage in the vicinity of an aluminum smelter in Norway, *Water Air and Soil Pollution*, **160**, 145–159.

RESULTS OF MEASUREMENTS OF SOIL ACTIVITY, SOIL GAS AND INDOOR RADON CONCENTRATIONS IN PRILEP AND SKOPJE

*Zdenka Stojanovska[1], Blazo Boev[2], Jovan Januseski[1] ,Mimoza Ristova[3]

[1] *Institute for Public Health of RM, Laboratory for Radioecology Skopje, Macedonia*
[2] *Faculty of Mining, Geology and Polytechnic, Goce Delcev University, Stip, Macedonia*
[3] *Physics Department, Faculty of Natural Sciences and Mathematics, University in Skopje, Macedonia*

Abstract: The preliminary measurements of radon and thoron concentrations in the soil gas were done, using short term active method. Field measurements were made at a distance of 1-2 m away from the randomly selected houses in Skopje and Prilep. Ten series of short-term (10-minutes) measurements were made. The arithmetic mean values of radon and thoron concentrations in the soil gas were found to be 15.9 ± 5.6 kBq m^{-3} and 5.3 ± 2.3 kBq m^{-3}, respectively. Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in soil were evaluated from gamma spectrometry analysis on the soil samples that were collected from the same locations. Indoor radon concentrations were measured in the houses of the same locations.

1. Introduction

Radioactivity is a part of our everyday's life and as such, it is present in every medium of the living environment. The study of radioactivity in the living environment is a crucial segment of radiation protection, but at the same time, it is a useful tool in the exploration of the transport processes which originate from the nature itself.

In the period of 2007-2009, a survey of natural radioactivity was carried out in whole regions of Republic of Macedonia (1-6). Attempts were made in all investigates areas to identify populations receiving elevated natural exposures that might serve as potential groups for a planned future health study.

From human perspective, indoor radon (^{222}Rn) and its progeny are one of the most significant natural sources of radiation exposure to the population. As an inert gas, radon freely diffuses through the soils and reaches the atmosphere where it could migrate into structure of dwellings to pose a health hazard. The national survey of indoor radon concentration in 2008 was done. Indoor radon concentration was measured in 413 dwellings by using CR-39 detectors, with a total 1652 measurements. Detectors were deployed in four seasons in living room or bedroom of each house, where inhabitants spent the most of the time (5,7).

Some researches even believe that measurements of radon in the soil gas can be used to predict indoor radon level. In addition, numerous activities in the field of radon measurements in soil have been published (8-11). In order to give a more comprehensive evaluation of exposure and to identify sources of indoor radon concentrations in Skopje and Prilep, some measurements in 16 dwellings were undertaken in 2010. In this paper, we report the results of these measurements, with the emphasis on their correlations.

2. Study area

In order to investigate the concentrations of ^{40}K, ^{226}Ra and ^{232}Th in soil, radon and thoron concentrations in the soil gas and indoor radon concentrations, as well as to test its correlations, 16 testing sites were selected randomly for this study. These sites are situated a two towns Prilep and Skopje.

* Corresponding author. Tel.: +389 2 3125044; fax: +389 2 3223354. E-mail address: stojanovskazdenka@gmail.com

3. Measuring procedure

3.1. Activity concentrations in the soil

The soil samples were collected on two different depths (0-20 cm and 20-100 cm). All samples were grinded and then dried at 105°C temperature until the moisture of the sample was completely evaporated. After homogenization, the samples were transferred in 500 ml Marinelli beaker which was used for the gamma spectrometry measurements. The containers were closed and sealed hermetically and kept aside for a month, in order to achieve a secular equilibrium between ^{226}Ra and its daughters.

The gamma spectrometry measurements were carried out with a p-type HPGe detector (Canberra Inc.; 25% relative efficiency, resolution of 1.79 keV at 1.33 MeV, 8192 ch. digital analyser, and with software GENIE 2000 for spectrum evaluation.

From the gamma spectrum the activity of the following radionuclides: ^{40}K, ^{226}Ra and ^{232}Th was determined. The activity of ^{40}K was determined from its 1460 keV line. The activity of ^{226}Ra was determined from the gamma lines associated with the short-lived daughters of: ^{214}Pb (295.22 keV, 351.93keV) and ^{214}Bi (609.31 keV, 1120.29 keV, 1764.49keV). Finally, the activity of ^{232}Th was determined from the gamma lines of ^{228}Ac (338.32 keV, 911.2 keV, 968.97 keV), ^{208}Tl (583.19 keV).

3.2. Indoor radon concentrations

The indoor radon concentration was measured at the same position locations during the four seasons (4 times a year with the same time of exposure, 3 months) in period 2008-2009.

The measurements were performed with commercially available RSKS passive track detectors. The detector consists of a CR-39 chip placed in a cylindrical diffusion chamber with dimensions 25 mm x 40 mm.

The detectors were set either in the living rooms or the bedrooms inside the houses, at a height of 1 to 1.5 m above the floor, at a distance greater than 0.5 m from each wall (to avoid influence of ^{220}Rn originating from the building materials, which contributes negligibly to the room interior, due to the low diffusion length) and, minimum 20 cm away from any other object in the room.

At the end of each seasonal cycle, the detectors were returned to the laboratory for analysis.

3.3. Radon and Thoron concentrations in soil gas

The measurement set-up consisted of the SARAD (RTM2100) radon monitor and soil gas sampling system. The RTM2100 - semiconductor detector combined with the alpha spectrometry analysis measured simultaneously radon and thoron concentrations by the short living daughter product (^{218}Po and ^{216}Po). The measurement locations were set at the house's courtyards for which the indoor concentrations of radon were measured as they were randomly selected, in Prilep and Skopje. Attention was payed that the selection was made from different town sections. The measurements in a selected location were made at a 1-2 m distance from each selected house.

A one meter (1 m) deep hole with 7 cm diameter was drilled. The soil sampler was carefully inserted into the bore-hole and connected directly to the instrument (connected to internal pump) by a flexible PVC tube. Ten series of short-term (10-minutes) measurements were made, and each result was recorded and kept for further processing.

4. Results and discussion

The results of the gamma spectrometry measurements of the soil samples, taken from holes on different depths (0-20 cm and 20-100 cm), are presented in Table 1. The activity concentration as well as the total combined uncertainty at the 68% confidence level of ^{40}K, ^{226}Ra and ^{232}Th are in Bq kg^{-1}.

The arithmetic mean (± standard deviation of the mean value) of the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th on the (0 - 20)cm were (585 ± 33) Bq kg^{-1}, (38 ± 3) Bq kg^{-1} and (38 ± 2) Bq kg^{-1}, respectively. The activity of ^{226}Ra ranges from 19 to 56 Bq kg^{-1} and from 20 to 57Bq kg^{-1} on the (0-20)cm and (20 – 100)cm deeps respectively The range of measured activity on the (0-20)cm of ^{232}Th was 24-52 Bq kg^{-1} and 26-53 Bq kg^{-1} on the 20-100cm deep. The ranges of measured activity of ^{40}K on the (0-20)cm and (20-100)cm deeps were ranged from 319 to 761 Bq kg^{-1} and 332 to 807 Bq kg^{-1}, respectively.

Table 1. Activity concentraction of ^{40}K, ^{226}Ra and ^{232}Th in soil samples

N	Location	0-20cm						20-100cm					
		^{40}K		^{226}Ra		^{232}Th		^{40}K		^{226}Ra		^{232}Th	
		A*	u(A)**	A	u(A)	A	u(A)	A	u(A)	A	u(A)	A	u(A)
1	Prilep	761	10	53	0,4	49	0,6	765	10	54	0,7	53	0,6
2	Prilep	576	8,0	42	0,4	36	0,5	611	8,3	42	0,4	37	0,5
3	Prilep	749	9,9	42	0,4	41	0,5	807	10	41	0,4	39	0,5
4	Prilep	685	9,2	44	0,4	43	0,5	707	9,4	43	0,4	47	0,5
5	Prilep	659	9,2	47	0,4	42	0,5	728	9,6	57	0,5	51	0,6
6	Prilep	682	9,3	56	0,5	52	0,6	731	9,5	52	0,4	49	0,5
7	Prilep	609	11	47	0,6	47	0,8	555	7,8	49	0,4	45	0,5
8	Prilep	732	9,7	52	0,4	52	0,6	727	9,7	49	0,4	48	0,6
9	Prilep	559	7,7	44	0,4	47	0,5	569	7,7	46	0,4	53	0,5
10	Skopje	505	7,5	22	0,3	30	0,5	491	30	21	0,4	31	0,7
11	Skopje	604	8,5	30	0,3	30	0,4	715	9,7	25	0,3	34	0,5
12	Skopje	625	8,6	38	0,4	33	0,5	639	8,6	35	0,3	32	0,5
13	Skopje	434	6,2	21	0,2	29	0,4	457	6,6	25	0,2	32	0,4
14	Skopje	379	5,9	31	0,3	24	0,4	403	6,4	25	0,3	26	0,4
15	Skopje	319	6,1	19	0,2	26	0,4	332	5,4	20	0,2	28	0,4
16	Skopje	488	7,5	25	0,3	29	0,4	488	7,5	25	0,3	38	0,5

*activity concentration in Bq kg^{-1}.
**total combined uncertainty (σ=1) Bq kg^{-1}.

It seems useful to examine the downward distribution for ^{40}K, ^{226}Ra and ^{232}Th in surface soil to obtain an insight into mixing near the surface. For this purpose, radioactivity ^{40}K, ^{226}Ra and ^{232}Th, was compared for each sample taken from the two depths of each hole (12). A nonparametric linear regression analysis was performed, and the Spearman correlation coefficient was 0.94 for ^{40}K, 0.96 for ^{226}Ra and 0.87 for ^{232}Th, at the level of significance p=0.05.

From the statistical analysis, the results of the gamma spectrometry analysis of the soil samples, taken from holes, showed statistically insignificant differences between activity concentration of ^{40}K, ^{226}Ra and ^{232}Th from different depths (0-20cm and 20-100cm). On Figure 1 are presented the mean values of ^{226}Ra and ^{232}Th at 0 -100 cm depth.

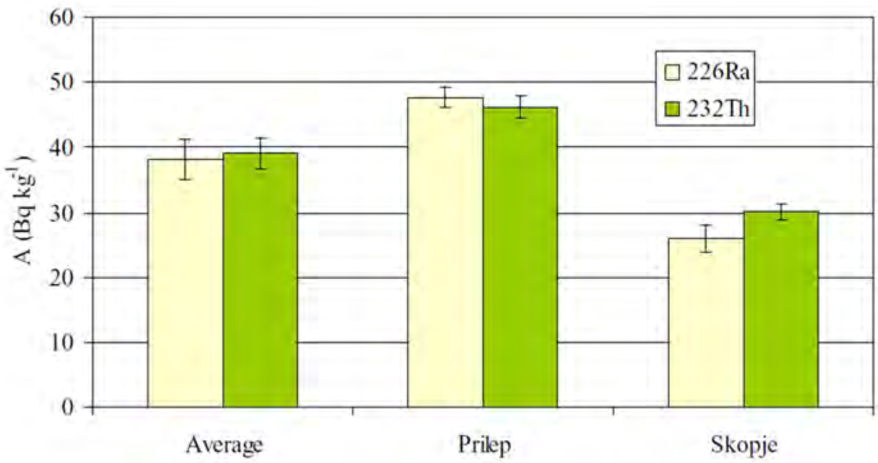


Figure 1. Mean values and 95% LSD intervals of the ^{226}Ra and ^{232}Th concentration at 0-100 cm depth

In Tabe 2, the results of indoor radon concentration measured in different season are present. The annual average indoor concentration is estimated as an arithmetic mean value of measured results in four seasons. All results are presented in Bq m^{-3}.

As can be seen from Table 2, the maximum value of radon concentration was 956 Bq m^{-3} and the minimum 16 Bq m^{-3} measured in winter and summer respectively. The indoor radon concentrations are subjected in seasonal variation. This could be attributed to the applied passive techniques, which are advantageous due to averaging of the seasonal variations caused by the long measurement period. The annual radon concentrations were ranged between 40 and 552 Bq m^{-3}.

Table 2. Results of indoor radon concentration ^{222}Rn

N	Location	^{222}Rn (Bq m^{-3})				
		Winter	Sping	Summer	Autumun	Annual average
1	Prilep	112	70	33	51	**66**
2	Prilep	300	221	117	198	**209**
3	Prilep	89	44	52	43	**57**
4	Prilep	117	95	41	69	**80**
5	Prilep	59	47	42	58	**51**
6	Prilep	323	178	73	154	**182**
7	Prilep	54	41	29	35	**40**
8	Prilep	72	79	64	43	**64**
9	Prilep	956	478	128	647	**552**
10	Skopje	45	51	16	50	**40**
11	Skopje	127	60	38	114	**85**
12	Skopje	335	157	171	301	**241**
13	Skopje	738	331	53	294	**354**
14	Skopje	291	173	38	293	**199**
15	Skopje	274	141	59	202	**169**
16	Skopje	104	49	39	94	**71**

The active method was used to determine the radon and thoron concentrations in the soil gas. The meteorological parameters: air temperature, pressure and relative humidity were measured with the same device because it is known that they can influence radon concentration. Therefore it seems important to know under what conditions the short-term radon measurements were carried out (13). The average values of air temperature, air pressure and relative air humidity ranged from 19 °C to 46 °C, 932 hPa to 980 hPa and 26% to 73%, respectively. The results of the soil gas measurements on the same locations are presented in Table 3.

Table 3. Radon and Thoron concentrations in soil gas

N	Location	^{222}Rn		^{220}Rn	
		C (kBq m^{-3})	u(C) (kBq m^{-3})	C (kBq m^{-3})	u(C) (kBq m^{-3})
1	Prilep	57,6	0,9	9,5	0,3
2	Prilep	23,4	0,4	5,2	0,2
3	Prilep	2,6	0,1	0,4	0,0
4	Prilep	3,3	0,1	2,5	0,1
5	Prilep	4,5	0,3	1,0	0,1
6	Prilep	3,7	0,2	0,5	0,1
7	Prilep	2,9	0,2	3,7	0,3
8	Prilep	2,8	0,1	2,2	0,1
9	Prilep	0,8	0,1	0,9	0,1
10	Skopje	20,7	0,4	38,6	0,1
11	Skopje	57,1	0,8	8,2	0,3
12	Skopje	62,5	0,7	7,3	0,2
13	Skopje	0,2	0,0	0,2	0,0
14	Skopje	6,1	0,2	1,4	0,1
15	Skopje	1,0	0,1	0,6	0,1
16	Skopje	5,0	0,2	2,5	0,1

The values of radon concentration in soil gas using short-term measurements obtainned using active devices varied from 0.2 kBq m^{-3} to 62.5 kBq m^{-3}. Obtained results for thoron concentrations in soil gas were found to vary from 0.2 kBq m^{-3} to 38.6 kBq m^{-3}. Nonparametric linear regression analysis of radon (^{222}Rn) and thoron (^{220}Rn) concentrations in soil gas has showed a statistically significant positive correlation with the Spearman correlation coefficient R=0.81 (p=0.0003). The mean values and 95% LSD intervals of the concentration of radon and thoron in soil gas are presented on the figure 2.

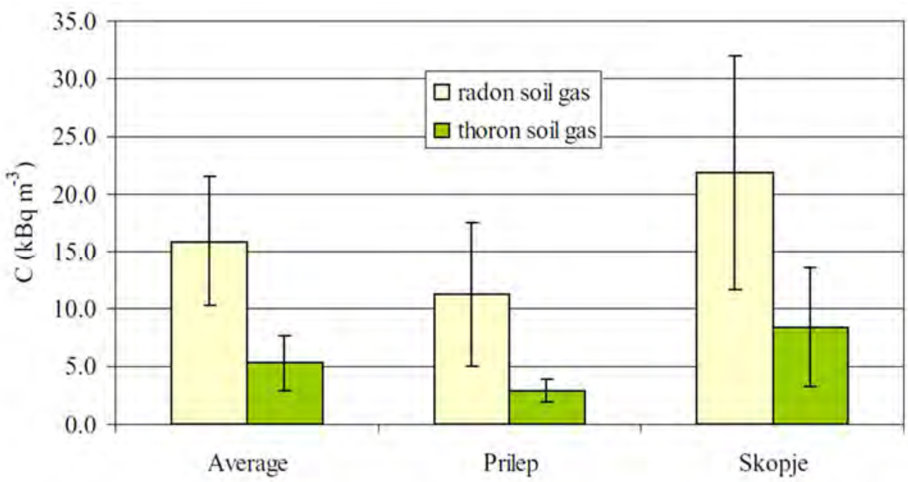


Fig. 2. Mean values and 95% LSD intervals of the radon and thoron concentration in soil gas

Furthermore the correlation between the ^{226}Ra content in the soil and the radon concentration in the soil gas were observed. There is no statistically significant correlation between radon concentration in soil gas and activity concentrations of ^{226}Ra in soil (p=0.805). Correlation between thoron (^{220}Rn) concentration in soil gas and soil activity concentrations of ^{232}Th, as well as correlation between the indoor radon concentration of and radon concentration in soil gas were statistically insignificant.

5. SUMMARY

A limited number of measurements of radon and thoron soil gas concentrations in the soil gas in Skopje and Prilep led to conclusion that there is a correlation between radon and thoron concentrations in soil gas, as well as a correlation between activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in soil is confirmed. Possibilities for other correlations are not excluded. However, the number of the data points is too small to allow generalization of the last conclusion. These results can be utilised to set up the methodology for a more systematic investigation to radon concentration in the soil gas.

6. REFERENCES

(1) Zdenka Stojanovska and Dusan Nedelkovski., Initial investigation of the natural radioactivity in the soil in some locations in Macedonia from radiation protection point of view. Physica Macedonica 58 (2008) 67-74.

(2) Димовска, С., 2007. Дистрибуција на некои природни и вештачки радионуклиди во почвата од Велес и неговата околина. Специјалистички труд, Хемиски институт, ПМФ, Скопје.

(3) Димовска, С., 2007. Радиоактивност на почвите од Кавадарци и неговата околина. Специјалистички труд, Хемиски институт, ПМФ, Скопје.

(4) Zdenka Stojanovska, Blazo Boev, Mimoza Ristova, Spatial Distribution of K, Th and U Elemental Concentrations in Soils of the Republic of Macedonia. 1-st International workshop on the UNESCO-IGCP Project (2011).

(5) Zdenka Stojanovska, Jovan Januseski, Blazo Boev, Mimoza Ristova,. Indoor exposure of population to radon in The FYR of Macedonia. Radiation Protection dosimetry (2011) 1-6.

(6) Zdenka Stojanovska, Nedelkovski Dusan, Jovan Janusevski.. Radon concentration in ground dwellings in winter/spring season and dose assessment in the citizens of Skopje. Archives of Public Health 1 (2009) 97-103.

(7) Zdenka Stojanovska, Jovan Januseski, Peter Bossew, Zora S. Zunic, Tore Tollefsen, Mimoza Ristova, Seasonal indoor radon concentration in FYR of Macedonia. Radiation measurement 46, (2011)602-610.

(8) Ngachin, M., Garavaglia, M., Giovani, C., Kwato Njock, M.G., Nourreddine, A., 2008. Radioactivity level and soil radon measurement of a volcanic area in Cameroon. Journal of Environmental Radioactivity 99 (2008) 1056-1060.

(9) Giovani, C., Cappelletto, C., Garavaglia, M., Scruzzi, E., Peressini, G., Villalta, R.,. Radon survey in schools in north-east Italy. Radiation Protection Dosimetry 97 (2001) 341-344.

(10) Jonsson, G., Baixeras, C., Devantier, R., Engel, W., Font,. L.L., Freyer, K., Ghose, R., Theutler, H.C.,. Soil radon level and measured with SSNTD's and soil radium content. Radiation Measurements 31 (1999) 291-294.

(11) Singh, S., Singh, B., Kumar, A., Natural radioactivity measurements in soil samples from Hamipur district. Radiation Measurements 36 (2003) 547-549.

(12) Fukui, M. Evaluation of Radon in Soil gas and natural radioactivity in surface soil of Kinki District, Japan. Journal of nuclear science and technology, 44 (2007) 1106-1116.

(13) Zunic, Z. S., Kobal, I., Vaupotič, J., Kozak, K., Mazur, J., Birovljev, A., Janik, M., Celikovicґ , I., Ujic, Demajo, A., Krsticґ , G., Jakupi, B., Quarto, M., Bochicchio, F.,. High natural radiation exposure in radon spa areas: a detailed field investigation in Niška Banja (Balkan Region). J. Environ. Radioact. (2006) 89, 249–26.

POLLUTION AROUND THE ZLETOVO MINE, REPUBLIC OF MACEDONIA

Goran Tasev and Todor Serafimovski

Faculty of Natural and Technical Sciences, University "Goce Delčev", Štip, Republic of Macedonia; goran.tasev@ugd.edu.mk; todor.serafimovski@ugd.edu.mk

Abstract: Increased environmental awareness about the anthropogenic input around the industrial facilities around the world induced the study of Zletovo Mine's influence to the adjacent environ. The study in fact have shown significant anthropogenic input to the soils and waters. Namely, concentrations of some heavy metals in both medias reached few times increased concentrations above the allowed values. In, waters of highest concern were concentrations of these metals: 0.028÷3.117 mg·kg^{-1} Pb, 0.049÷16.735 mg·kg^{-1} Zn, 0.004÷0.228 mg·kg^{-1} Cd, 0.005÷0.998 mg·kg^{-1} Cu and 0.09÷22.84 mg·kg^{-1} Mn while in soils the most significant were those of the following metals: 42.30÷529.66 mg·kg^{-1} Pb, 138÷3290 mg·kg^{-1} Zn, 24.3÷72.6 g·kg^{-1} Fe and 643÷28000 mg·kg^{-1} Mn.

Key words: Zletovo Mine, ore, waste, heavy metals, pollution, water, soil,

Introduction

Mine wastes represent the greatest proportion of waste produced by industrial activity. In fact, the quantity of solid mine waste and the quantity of Earth's materials moved by fundamental global geological processes are of the same order of magnitude or approximately several thousand million tonnes per year (Fyfe 1981; Förstner 1999). Opposite to the fundamental global geological processes such as oceanic crust formation, soil erosion, sediment discharge to the oceans, and mountain building, which naturally move Earth's materials around the Earth's crust and shape our planet, the human extracts material from the Earth during mining and discards most of the extracted crust as waste. The modern mining industry is of considerable importance to the world economy as it provides a great diversity of mineral products for industrial and household consumers. The consequence of the large size of the mining and mineral processing industry is not only the large volume of materials processed but also the large volume of wastes produced (Younger, 2000; Younger et al., 2000). There lies the reason, why we have proceeded with study around one of the oldest Macedonian mines and eventual determination of its environmental impact to the adjacent vicinity indicated by Alderton et al. (2005), Dolenec et al. (2005) and Dolenec et al. (2007).

The Zletovo Pb-Zn Deposit short facts

The Zletovo mine is located in the vicinity of the city of Probistip, Macedonia. The mine started operation in 1940 and its production lasts until today with certain short-term interruptions. As it is well known the mineralization is related to Tertiary calcalkaline magmatic rocks, mostly dacites and andesites. Mineralization is found in a dacitic volcano-sedimentary suite that has been altered to clays and micas (Serafimovski and Aleksandrov 1995; Serafimovski and Boev 1996). The main ore mineral association is composed of galena and sphalerite, followed by tetrahedrite, pyrrhotite, magnetite, chalcopyrite, pyrite, and Mn oxides are also common. Production during certain periods have reached 300 000 t of ore per annum, with ore grades higher than 9% Pb and 2% Zn, and significant concentrations of Ag, Bi, Cd, and Cu. Ore was concentrated by flotation at Probistip and tailings were disposed of in two impoundments situated in adjacent river and stream valleys. One of them, the river Kiselica, drains the flotation plant at Probistip while the Koritnica River drains the area containing the main workings of the Zletovo mine (Figure 1).

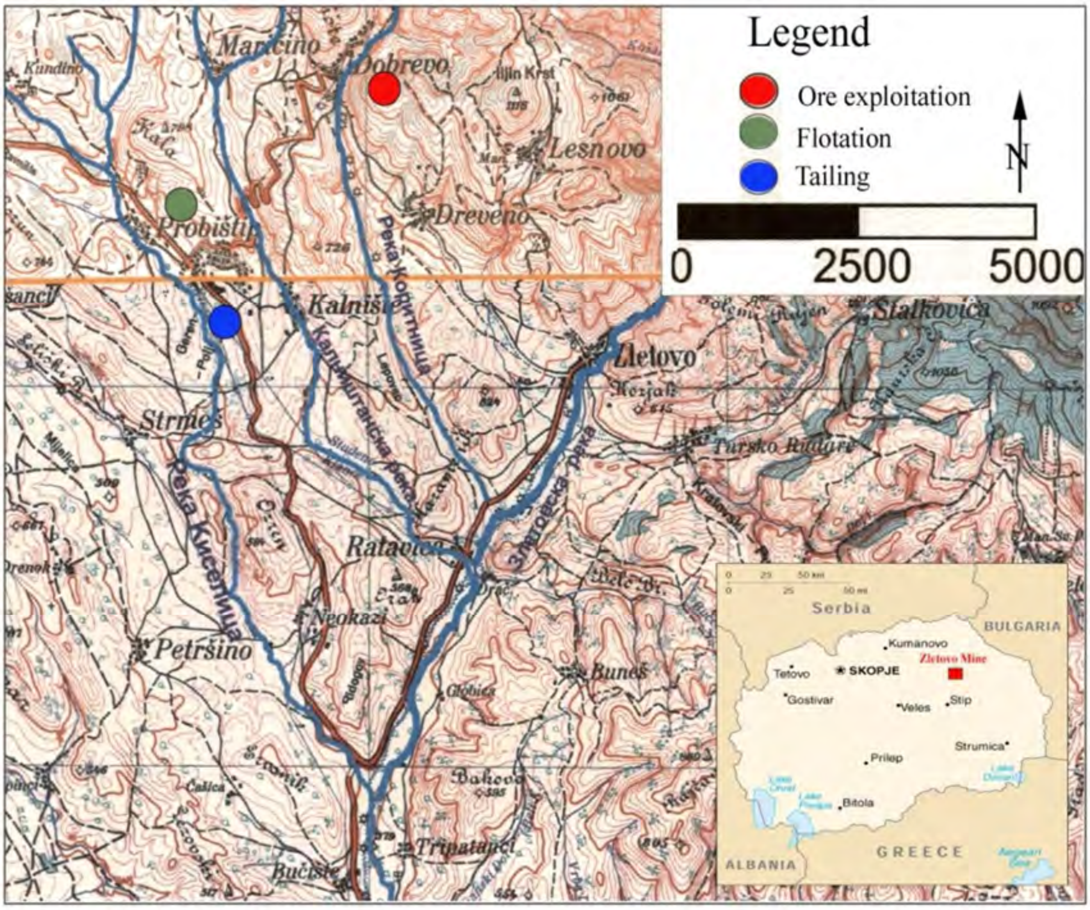


Fig. 1. Main sources of heavy metals pollution induced by work of Zletovo Mine, Macedonia

Both of these rivers join the River Zletovska, which flows down to inflow into the River Bregalnica.

Sampling area and methods

At each location, streams were sampled in their central parts to assess the contributions of the drainage from the mining activities. Samples were taken progressively downstream, and in some locations, in receiving waters. All the streams sampled close to the mine were small first or second order streams. Receiving waters were larger rivers, and samples were taken downstream of the confluence. Sampling density varied from a few metres to several kilometres, depending on the situation; in general, sampling density was lower further downstream.

The main locations that have been sampled were at the drainage systems of Zletovo, Koritnica River, Globica, Kiselica, Strmos, Buciste, Ziganci and Ularci as well as sites around these streams-rivers. Water was collected in polythene syringes, passed through a

0.45µm filter and transferred into polythene tubes. Water was acidified with 0.4 ml of 50% nitric acid. Conductivity and pH and were measured in the field for all water samples. Soil samples were also collected at several locations, but in general perpendicular to the stream-river flows. For these, a hot (80°C) concentrated nitric acid digest was used to leach elements from the soil.

Solutions were analysed by ICP-AES or ICP-MS, depending on concentrations. A large number of analytes were determined but only those that are likely mining related and environmentally significant are presented and discussed here. The concentrations were compared to reference guidelines to assess their significance.

Results and discussion

The results from analyses of water samples are shown in Table 1.

Table 1. Concentrations of particular heavy metals in water samples from the vicinity of the Zletovo Mine, Macedonia (maximums in red, minimums in blue color)

sample	Pb (mg/l)	Zn (mg/l)	Cd (mg/l)	Cu (mg/l)	Fe (mg/l)
ZN-1	0,028	0,057	0,004	0,005	0,123
ZN-2	0,065	0,157	0,011	0,121	0,896
ZN-3	0,064	0,665	0,013	0,042	0,725
ZN-4	0,548	12,304	0,068	0,998	22,84
ZN-5	0,048	0,078	0,004	0,026	0,32
ZN-6	0,278	1,116	0,051	0,143	1,435
ZN-7	0,143	1,298	0,011	0,042	0,333
ZN-8	3,117	13,978	0,228	0,712	6,998
ZN-9	0,161	1,099	0,011	0,033	0,487
ZN-10	0,867	16,735	0,225	0,343	6,538
ZN-11	0,112	0,296	0,009	0,023	0,223
ZN-12	1,623	2,615	0,198	0,167	1,336
ZN-13	0,035	0,049	0,004	0,027	0,09
ZN-14	0,436	0,689	0,198	0,138	0,856
ZN-15	0,098	0,083	0,006	0,009	0,231
ZN-16	0,198	0,534	0,168	0,198	0,862
MDK_{std}	0,01	0,1	0,0001	0,01	0,3

As can be seen from the table above in waters of highest concern were concentrations of lead, which ranged from 0.028 up to 3.117 $mg \cdot kg^{-1}$ Pb (Figure 2a). Calculated factor for it have shown an average value of 48.88, which is significantly high. The highest concentrations were recorded at Kiselica river and near the Buciste location. The latest is probably due to water draining from the the flotation dam. In regards of zinc concentrations it was determined range of 0.049÷16.735 $mg \cdot kg^{-1}$ Zn (Figure 2b), of which the highest were determined in Koritnica River, Kiselica and close to the Strmos, as a direct consequence of mine exploitation and flotation processes. The enrichment factors for this metal have shown an average value of 34.35. Cadmium concentrations were in the range 0.004÷0.228 mg·kg^{-1} Cd (Figure 2c) and with the highest enrichment factor (755.63) of all the analyzed heavy metals in the water samples. Especially high were the concentrations at Kiselica River, Strmos and Buciste.

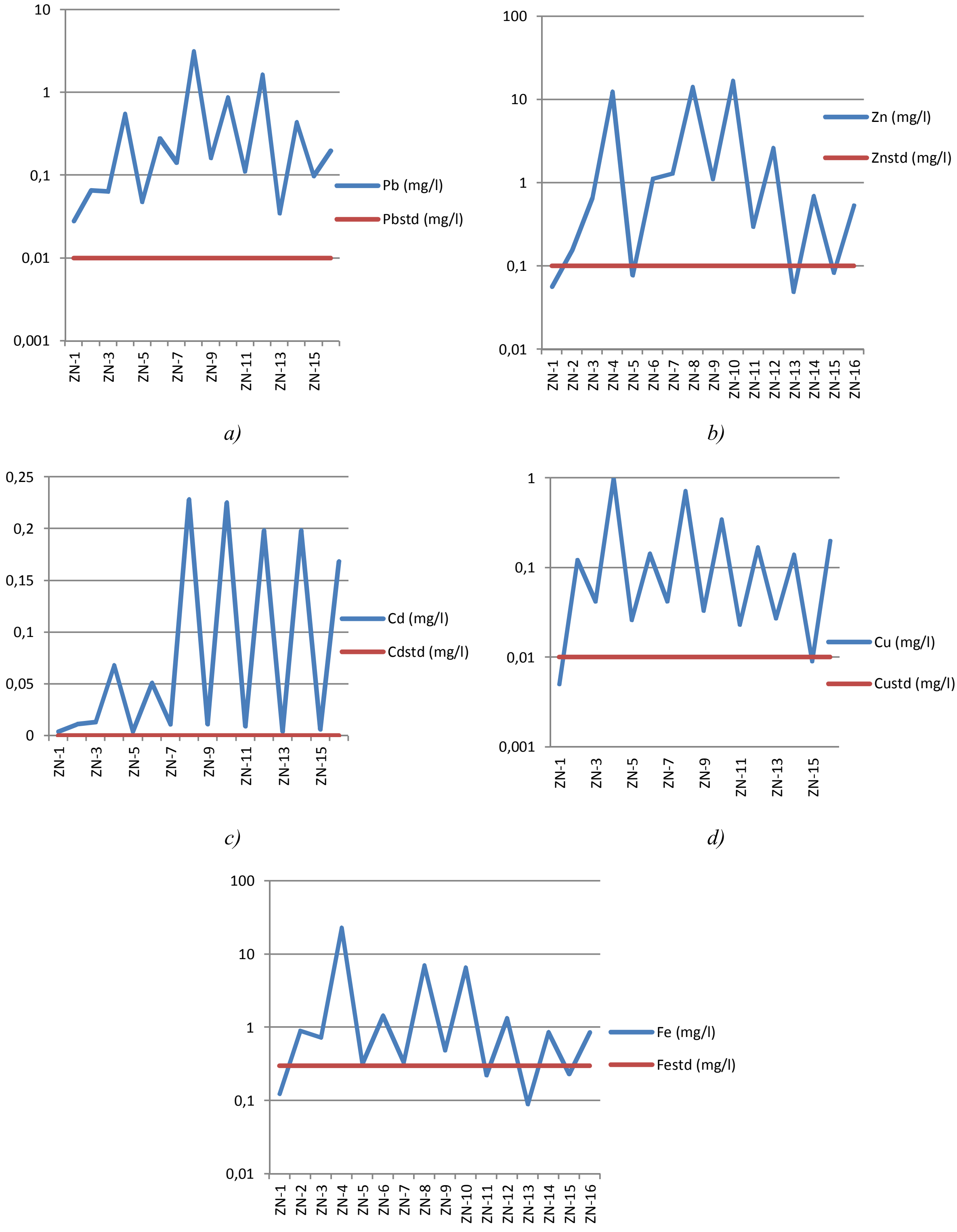


Fig. 2. Measured concentrations of some heavy metals vs. standard values in waters in the vicinity of the Zletovo Mine, Macedonia
(Note: *a, b, d* and *e* plots have logarithmic vertical scale)

As far as copper concentrations are concerned we have to stress out that they ranged from 0.005 up to 0.998 $mg \cdot kg^{-1}$ Cu (Figure 2d), with highest of them at the Strmos and Kiselica River, and calculated enrichment factor of 18.92. Copper concentrations are the most probably due to effluents from the floatation as well as acid drainage. Iron concentrations were in the range 0.09÷22.84 $g \cdot kg^{-1}$ Fe. Its enrichment factors averaged relatively low 9.23, pointing out to a low pollution intensity with this metal.

Soils results complemented those of waters and obtained values are given at Table 2.

Table 2. Concentrations of particular heavy metals in soil samples from the vicinity of the Zletovo Mine, Macedonia (maximums in red, minimums in blue color)

Sample	Pb (mg/kg)	Zn (mg/kg)	Fe (g/kg)	Mn (mg/kg)
ZN-1	42,3	138	19,3	643
ZN-2	102	283	29,66	1980
ZN-3	153	163	31,66	8680
ZN-4	529,66	2300	44,5	8553
ZN-5	389	1800	29,45	5920
ZN-6	201	300	31,23	1842
ZN-7	116,3	298	29,36	2016
ZN-8	192	420	42,36	2090
ZN-9	209	265	37,89	2312
ZN-10	493,8	2333	61	28000
ZN-11	435	2400	61,12	5440
ZN-12	333	1390	37,45	8666
ZN-13	480	2320	76,9	4350
ZN-14	358	3007	63,32	21560
ZN-15	443	3240	55,22	18960
ZN-16	211	444	29,45	3320
ZN-17	198	489	31,22	5550
ZN-18	211	611	29,33	2750
ZN-19	283	1230	33,71	2630
ZN-20	233	1120	30,16	2610
ZN-21	229	1326	31,78	2590
ZN-22	190	745	34,23	6870
ZN-23	165	796	29,97	7540
ZN-24	200	910	28,63	6110
MDK	16	48	18	330

As it is obvious from the table above, we would like to stress out that lead values ranged from the 42.30÷529.66 $mg \cdot kg^{-1}$ Pb (Figure 3a), while the lowest values were determined near the Zletovo village the highest ones were determined in samples from localities Koritnica, Kiselica and Strmos. Calculated enrichment factor and index of geo-accumulation were 16.66 and 0.327, respectively. The highest concentrations of zinc were determined near the Koritnica, Kiselica and Ziganci while the whole range was quite wide starting from 138 mg·kg^{-1} Zn and ending up to 3240 mg·kg^{-1} Zn (Figure 2b) with enrichment factor of 24.60 and index of geo-accumulation of 0.135.

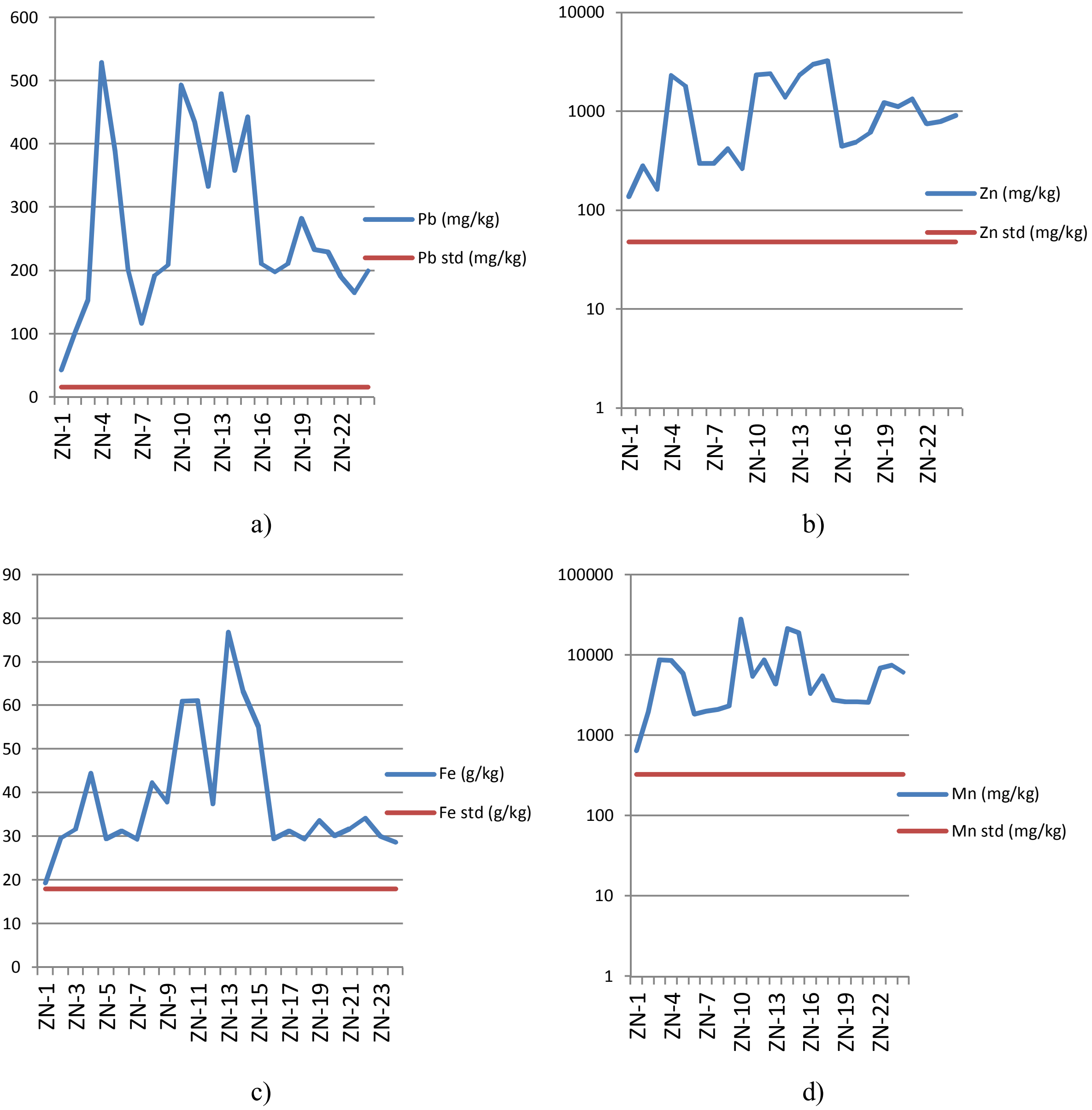


Fig. 3. Measured concentrations of some heavy metals vs. standard values in soils in the vicinity of the Zletovo Mine, Macedonia
(Note: *b* and *d* plots have logarithmic vertical scale)

Iron concentrations were narrower and within the range of 24.3÷72.6 g·kg^{-1} Fe. Either the iron haven't shown significantly increased values, the highest ones were recored for the locations such as Kiselica, Koritnica and Strmos. Also, for iron were calculated enrichment factor of 2.15 and index of geo-accumulation of 0.193. At last but not least the manganese have shown the highest concentrations among analyzed elements, ranging from 643 up to 28000 mg·kg^{-1} Mn. Calculated enrichment factor was of respectable 20.33 while the index of geo-accumulation was 0.0246.

Conclusion

The Zletevo Pb-Zn mine discharges low pH water that has high levels of several metals, including Al, Zn, Cd, and Fe; sediment concentrations are grossly elevated for several km downstream. In that context we would like to stress out that concentrations of particular have reached quite high values such are those of lead up to 3.117 $mg\cdot kg^{-1}$ Pb, zinc up to 16.735 $mg\cdot kg^{-1}$ Zn, cadmium up to 0.228 $mg\cdot kg^{-1}$ Cd, copper up to 0.998 $mg\cdot kg^{-1}$ Cu and manganese up to 22.84 $mg\cdot kg^{-1}$ Mn in waters while in soils the most significant were those of lead with up to 529.66 $mg\cdot kg^{-1}$ Pb, zinc up to 3290 $mg\cdot kg^{-1}$ Zn, iron up to 72.6 $g\cdot kg^{-1}$ Fe and manganese up to 28000 $mg\cdot kg^{-1}$ Mn. All of them have induced an idea of further analysis, monitoring and suggestion of eventual remediation procedures.

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.

Dolenec, T., Dolenec, M., Serafimovski, T., Dobnikar, M., Tasev, G. and Pivko, B., 2005: Influence of mining related activity on heavy metals in water and sediment from the Kalimanci Lake (NE Macedonia). Mineral Deposit Research: Meeting the Global Challenge, *Ed.Jingwen Mao and Frank P. Bierlein*. 8th SGA Biennial Meeting,Beijing, China, pp. 840-845.

Dolenec, T., Serafimovski, T., Tasev, G., Dobnikar, M., Dolenec, M. and Rogan, N., 2007. Major and trace elements in paddy soil contaminated by Pb–Zn mining: a case study of Kocani Field, Macedonia. *Environ Geochem Health (207) 29, pp. 21-32*

Förstner, U., 1999. Introduction. In: Azcue JM (ed) Environmental impacts of mining activities: emphasis on mitigation and remedial measures. Springer, Berlin-New York, pp 1-3

Fyfe, W. S., 1981. The environmental crisis: quantifying geosphere interactions. Science 213:105–110.

Hill S.J., 1992. Lead. In: Stoeppler, M. (ed.): Hazardous metal in the environment, 231-255, Elsevier, Amsterdam.

Serafimovski, T. and Aleksandrov, M., 1995. Lead-zinc deposits and occurrences in the Republic of Macedonia. Faculty of Mining and Geology Special issue no. 4, Stip, 387 pp (in Macedonian)

Serafimovski, T. and Boev, B., 1996. Metallogeny of the Kratovo-Zletovo volcano-intrusive complex. In: Knezevic V, Krstic B [Eds] Terranes of Serbia, Proc. UNESCO-IGCP project no. 356, Plate Tectonics of the Alpine metallogeny in the Carpatho-Balkan region, Belgrade, p 347-352.

Younger, P.L., 2002. *Mine water pollution from Kernow to Kwazulu-Natal: geochemical remedial options and their selection in practice.* Geoscience in south-west England, 10, 255-266

Younger, P.L, Banwart, S.A and Hedin, R.S., 2002. *Mine Water: Hydrology, Pollution, Remediation*, Kluwer Academic Publishers, Dordrecht.

LIST OF PARTICIPANTS

Ana Čobić	ancobic@geol.pmf.hr	CRO
Biljana Balabanova	biljana.balabanova@ugd.edu.mk	MKD
Blazo Boev	blazo.boev@ugd.edu.mk	MKD
Dragana Dogančić	dragana.dogancic@gfv.hr	CRO
Goran Tasev	goran.tasev@ugd.edu.mk	MKD
Goran Kniewald	kniewald@irb.hr	CRO
Jasmina Obhođaš	Jasmina.Obhodjas@irb.hr	CRO
Jasna Hrenović	jasnah@zg.biol.pmf.hr	CRO
Jovan Januševski	jovanjanuseski@yahoo.com	MKD
Katerina Bačeva	k.baceva@gmail.com	MKD
Ladislav Palinkaš	lpalinkas@geol.pmf.hr	CRO
Maja Kuzmanović	sabina.strmic@inet.hr	CRO
Matej Dolenec	matej.dolenec@ntf.uni-lj.si	SLO
Maša Martinić	sabina.strmic@inet.hr	CRO
Milihate Aliu	melihatealiu@hotmail.com	KOS
Mimoza Ristova	mristova@iunona.pmf.ukim.edu.mk	MKD
Nastja Rogan Šmuc	nastja.rogan@guest.arnes.si	SLO
Petra Vrhovnik	petra.vrhovnik@gmail.com	SLO
Predrag Tepeš	ptepes@gfv.hr	CRO
Robert Šajn	robert.sajn@geo-zs.si	SLO
Sabina Strmić Palinkaš	sabina.strmic@inet.hr	CRO
Šorša Ajka	ajka.sorsa@hgi-cgs.hr	CRO
Štefica Kampić	skampic@geol.pmf.hr	CRO
Tadej Dolenec	tadej.dolenec@ntf.uni-lj.si	SLO
Tena Šijakova-Ivanova	tena.ivanova@ugd.edu.mk	MKD
Todor Serafimovski	todor.serafimovski@ugd.edu.mk	MKD
Trajče Stafilov	trajcest@iunona.pmf.ukim.edu.mk	MKD
Vladimir Bermanec	vberman@public.carnet.hr	CRO
Vladimir Zebec	vladimir.zebec@hpm.hr	CRO
Zdenka Stojanovska	stojanovskazdenka@gmail.com	MKD
Željka Žigovečki Gobac	zeljkaz@geol.pmf.hr	CRO