

## Cooperation of GeoZS in geochemical investigation in former Yugoslavia

### Vključenost GeoZS v geokemične raziskave v nekdanji Jugoslaviji

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**Abstract:** The main purpose of this paper is to present geochemical investigations in former Yugoslavia. Intensively, in the last decade Geological Survey of Slovenia (GeoZS) spread the geochemical researches to Bosnia and Herzegovina, Macedonia, Croatia, Kosovo and Serbia through many bilateral projects. The main mines, smelters and ironworks were the main target of investigation. According to fact that Slovenia is very rich with mines, and consequently with numerous ironworks and smelters, the GeoZS has a long tradition in this kind of researches. Successful cooperation between GeoZS and institutions from other countries resulted by numerous publications, especially with Macedonia. Some of our results are already published, but still some remains unpublished. For determination of contamination, various sampling materials such as soil, alluvial sediments, river sediments, attic dust, lichen and moss were collected. In data processing various techniques of statistical approach have been used, but for their visualization also for the preparation of predictive maps of contamination we used universal kriging method, double kriging method and artificial neural network (ANN).

**Izveleček:** Glavni namen prispevka je predstaviti geokemične raziskave v nekdanji Jugoslaviji. V zadnjem desetletju Geološki zavod Slovenije (GeoZS) uspešno sodeluje pri številnih geokemičnih raziskavah v Bosni in Hercegovini, Makedoniji, na Hrvaškem, Kosovu in v Srbiji na osnovi številnih bilateralnih in evropskih projektov. Glavno cilj raziskav je bilo stanje okolja v okolici večjih rudnikov, topilnic kovin

in železarn. Glede na dejstvo, da je v Sloveniji delovalo večje število rudnikov ter posledično številne železarne in topilnice kovin, ima GeoZS dolgo tradicijo tovrstnih raziskav. Uspešno sodelovanje med GeoZS in ustanovami iz drugih držav je rezultiralo s številnimi objavami, kar posebej velja za sodelovanje z Makedonijo. Za določitev obremenjenosti okolja so bili zbrani različni vzorčni materiali, kot so tla, aluvialni in rečni sedimenti, podstrešni prah, lišaji in mahovi. V postopku obdelave podatkov so bile uporabljene napredne multivariantne statistične metode, za napoved razširjanja onesnaženja in vizualizacijo pa metode univerzalnega in segmentnega krigiranja, kakor tudi metode umetne inteligence (ANN – večslojni perceptron).

**Key words:** atmospheric contamination; river transport; heavy metals, former Yugoslavia

**Ključne besede:** težke kovine, onesnaženje, nekdanja Jugoslavija

## INTRODUCTION

This study represents a summary of environmental geochemical researches in the countries formed by breakup of Yugoslavia. Our researches are mainly focused on mining and metallurgical processes which are obviously the biggest destructors of environment: B&H (Ironworks Zenica; Ironworks Vareš and Fe mines - Smreka, Droškovac, Brezik, Pb-Zn-Ba mine Veovača); Croatia (the Drava valley; Experimental geochemical map of Slovenia and Croatia); Kosovo (Pb- Zn mine Trepča and Pb smelter Zvečan–Kosovska Mitrovica); Macedonia (Cu mine Bučim, Pb-Zn mines SASA and Toranica, As-Sb-Tl mine Alšar), Pb smelter Veles; FeNi – Kavadarci; thermoelectric power plants (Kičevo and Bitola), alluvial deposits of the Vardar river, Skopje);

Srbija (Mine and flotation Bor). After mineral extraction a big amount of waste has been exposed to oxidation conditions on the surface which lead to mobilisation of toxic material and formation of acidic water. Consequences of smelting and metallurgic processes are gaseous and atmospheric particles emission, waste water and waste mineral deposits.

The results help us to determine local and regional geochemical conditions, allowing us to understand a main processes and causes of the environmental changes and finally their contribution to the sustainable spatial planning. Obtaining and interpreting utilization data about chemical composition can be used in environmental protection and sustainable development of particular country, as well as for determina-

tion of pollution impacts to the human health, agriculture, forestry and future land use. Comprehensive approaches in investigation, understanding environmental issues, natural background and human impact on the environment is very important for development in earth and environmental sciences.

Basically, the major goals are strengthening an international scientific cooperation network and partnership between GeoZS and other former Yugoslav countries, improvement of material research standards, exploiting the research and technological demonstration results as well promoting the GeoZS to regional centres of excellence.

The results of numerous geochemical studies of natural distribution and proportion of anthropogenic heavy metals in the environment, especially in areas of former mining and smelting in Slovenia and the region can be used as guiding principles for the future environmental remedial actions.

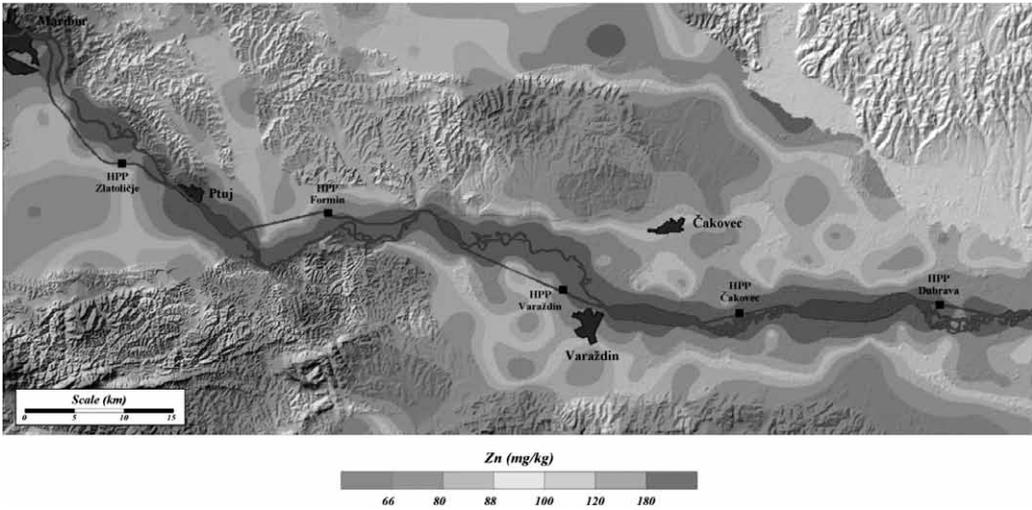
Specifically, the results from the entire study will complement our knowledge about a complexity of chemical compounds in the environment. Special emphasis is given to the further development of advanced data processing techniques and methods of linear and nonlinear mathematical models, based on the application of modern mathematical analysis such as PCA (Prin-

cipal Component Analysis), and ANN (Artificial Neural Network) at the distribution and transport of heavy metals in the environment.

#### **DRAVA VALLEY (SLOVENIA AND CROATIA)**

The Drava watershed, including its tributaries, has been an important mining and smelting region since antiquity. The industry underwent significant development during the middle Ages, and achieved its peak in the middle of the last century. Numerous mines and smelters such as Bleiberg-Kreuth in Austria, Cave del Predil in Italy and Mežica in Slovenia have had a significant impact on the chemical composition of the alluvial sediments of the Drava. It is widely known that the broader Drava valley is rich with heavy metals (Pb, Zn, Cu, As, Cd).

The study area covers the course of the Drava from the Slovenian-Austrian border which can be divided into two regions: Alpine and Pannonian. The Alpine region occupies the Drava canyon from the Slovenian-Austrian border up to the town of Maribor (about 78 km) where the Alpine landscape is dominant. The Pannonian region occupies an area from the town of Maribor downstream to the confluence of the Mura and Drava rivers, where the river valley is wide and exhibits the mor-



**Figure 1.** Spatial distribution of zinc in the Drava valley - Pannonian area (Croatia and Slovenia)

phological characteristics of the Pannonian basin. The Pannonian section of the study area covers about 123 km of the river flow. Throughout the study area, extensive deposits of alluvial sediments are found: in currently flooded zones (at present mainly behind the bank systems) covering about 55 km<sup>2</sup> in historically or periodically flooded areas (in recent times protected by the bulks, where agriculture production is intensive) covering about 100 km<sup>2</sup>; and sediments of alluvial terraces comprising an area of 930 km<sup>2</sup> (PEH et al., 2008; ŠAJN et al., 2011).

Across the Alpine region, the 16 sampling locations are defined at places along the river course where alluvial plains and river terraces occur. Simultaneously, samples of stream sediment

were collected at 8 points in the river. In the Pannonian part of the study area, where extensive alluvial plane and river terraces occur, 118 sampling locations at 25 profile lines were placed perpendicular to the river course. Analysis of 41 chemical elements was performed.

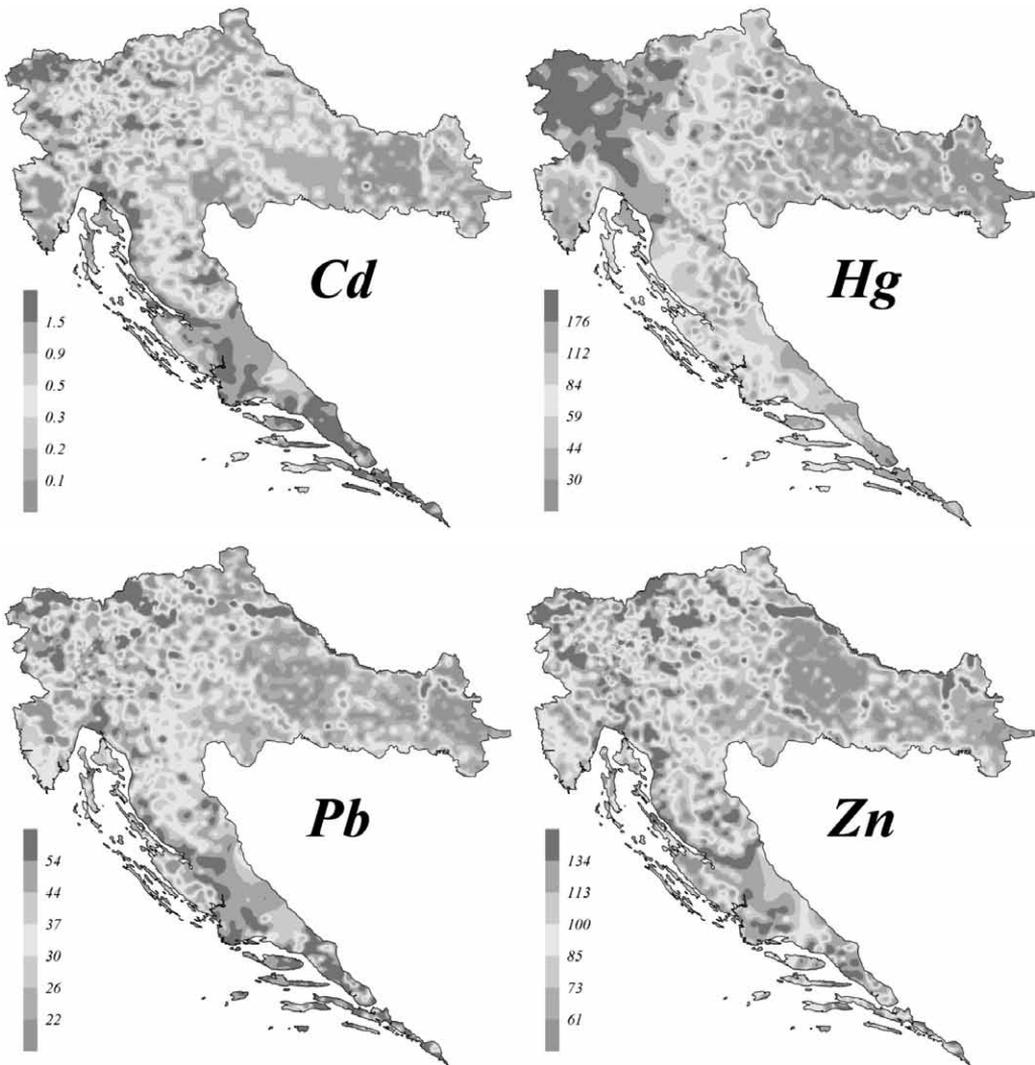
Based on a comparison of statistical parameters, spatial distribution of particular elements and the results of factor analysis, three natural and one anthropogenic geochemical associations were identified. The natural geochemical associations (Al-Fe-K-Co-Cr-Cu-Li-Ni-Rb-Sc-Th, Ti-Ce-La-Nb-Ta and Ca-Mg-Sr) were influenced mainly by lithology. The anthropogenic association (As-Ba-Cd-Mo-Pb-Sb-Zn) is mostly the result of historical zinc and lead mining and smelting in the Drava river watershed.

The entire assessed area of about 133 km<sup>2</sup> is, according to Slovenian and Croatian legislation, critically polluted with heavy metals, especially zinc. Based research of all forms of environmental pollution, including mines, smelters and ironworks in Slovenia at the present time, we have found that 88 km<sup>2</sup> of the total surface of the country is critically polluted with heavy metals. This means that alluvial sediments of the Drava River represent a wider source of pollution in both Slovenia and Croatia (PEH et al., 2008; ŠAJN et al., 2011).

#### EXPERIMENTAL GEOCHEMICAL MAP (SLOVENIA AND CROATIA)

Geochemical research of soil, stream and overbank sediments, as well as rocks in Slovenia and Croatia has been carried out continuously within the last two decades. The experimental geochemical map of Croatia and Slovenia is created as a result of successful international cooperation in the field of environmental geochemistry. Regarding the fact that strategy and methodology in producing our national geochemical maps have hitherto much in common we decided to produce the joint geochemical map explaining the geochemical trends of the wider area in a more comprehensive way (ŠAJN et al., 2006; ŠAJN et al., 2008)

The high contents of Fe, Ni, Cr, Sc, V, Mn, Al and Cu, have found in the areas covered by Pg and Cretaceous flysch, and in the areas of Neogene postorogenic sedimentary formations as well as by metamorphic rocks of the Pohorje Mt. and its environs. Nb, La, Th, As, Y and Zr are characteristic for brown carbonate soils, or terra rossa on carbonate platforms, as well as for the areas of eastern Slavonia. Ba, K and Na are typical for areas covered by igneous rocks. Ca, Sr, Mg and P are the most poorly differentiated and are associated either with rendzinas and similar soil types in the mountainous areas or, again, with the carbonate contents in immature alluvial soils in the Sava and Drava river valleys. Pb, Zn, Hg and Cd represents a typical heavy metal association originated either as a consequence of natural erosion of ore-bearing rocks or, again, of mining activity and smelting industry in the past. Their highest concentrations can be found in Slovenia in the vicinity of mines and metallurgic centers (Idrija, Mežica, Litija, Jesenice and Celje). Mining activity left its traces as well, which is reflected in the higher concentrations of heavy metals in recent sediments of the Sava and Drava rivers. Increased values in the areas of Gorski kotar, Velebit and Dalmatia derive their origin mostly from atmospheric deposition (Figure 2).

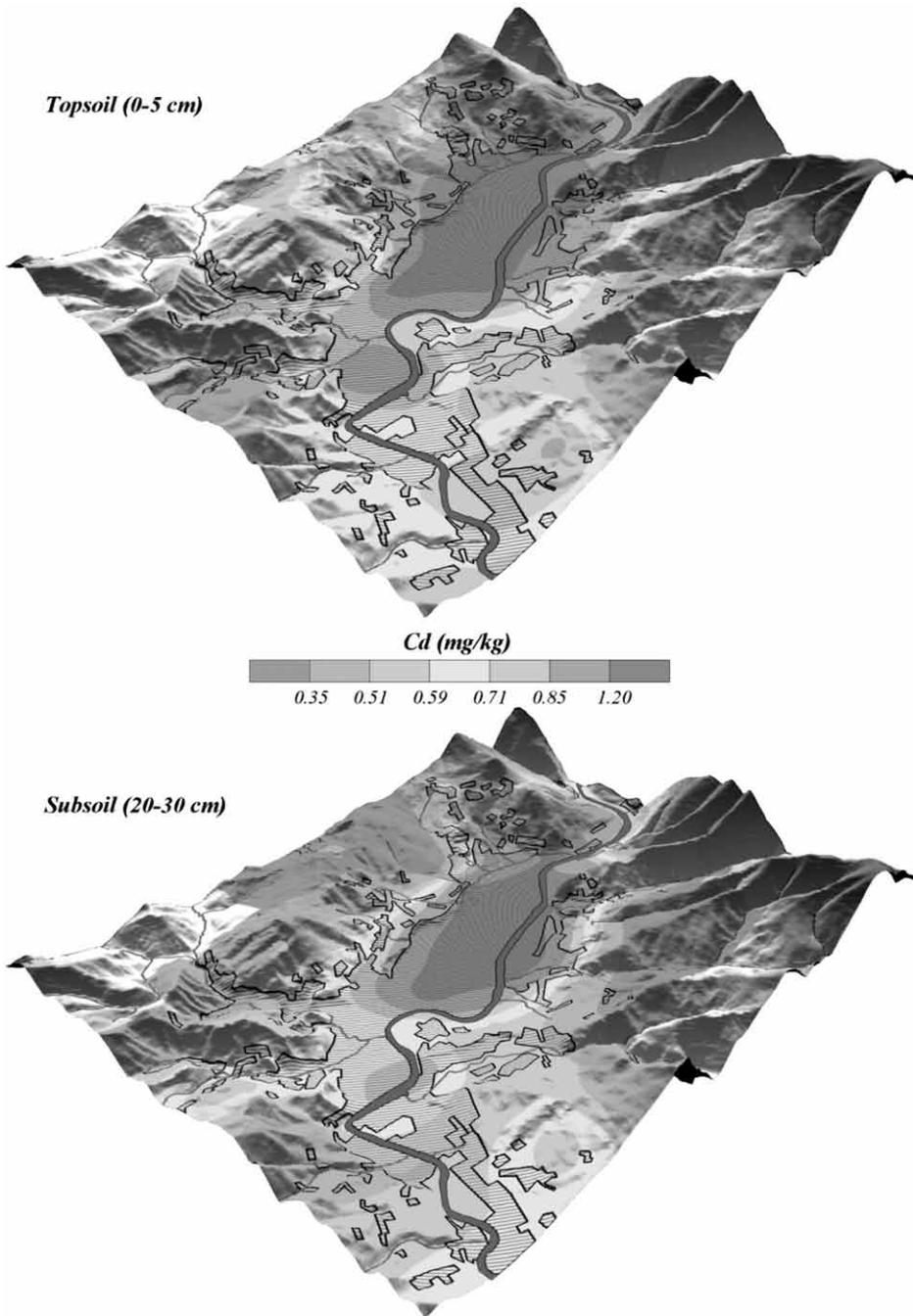


**Figure 2.** Spatial distribution of Cd, Hg, Pb and Zn in topsoil (Croatia and Slovenia)

### ZENICA (BOSNIA AND HERZEGOVINA)

Zenica, 170 000 inhabitants, is located in the valley of river Bosna, about 70 km north from Sarajevo. Construction of the iron and steel works started in

1892, during Austro-Hungarian period, and until the end of 50's, becomes the biggest construction site in the former Yugoslavia. Expansion of production reached the record of 1.72 Mt of pig iron and 1.91 million tons of crude



**Figure 3.** Spatial distribution of cadmium in the topsoil and the subsoil (Zenica, B&H)

steel in 1986. At the beginning of 90's production was completely stopped but production was continued with less capacity at the end of last century.

Area of 52 km<sup>2</sup> is covered with sampling grid that includes: urban zone, industrial zone and wider valley of the River Bosna. The entire area is separated into cells by the sampling grid with a density of sample per square kilometer but in the urban zone, sampling density is increased. At 62 different sites, 124 samples of topsoil (0–5 cm) and subsoil (20–30 cm) were collected

Two geogenic and one anthropogenic geochemical association are established on the basis of: visually indicated similarity of geographic distribution of elemental patterns in the topsoil and bottom soil, comparisons of basic statistics, correlation coefficient matrices, results of cluster and factor analyses and comparisons of enrichment ratios (ALIJAGIĆ & ŠAJN, 2006; ALIJAGIĆ, 2008; ALIJAGIĆ & ŠAJN, 2010).

Two natural geochemical associations (Al, Ca, Ce, K, La, Li, Nb, Rb, Sc, Ta, Ti Th, V and Y) and (Co, Cr, Na, Ni and Mg) are influenced mainly by lithology, but the third anthropogenic association (Ag, Bi, Cd, Cu, Hg, Mo, Pb, Sb and Zn) is result of historical activities of the ironworks Zenica, but also coal mining and other anthropogenic influences in the past.

High concentrations of Co, Cr and Ni are result of weathering processes and critical level of the mentioned elements is found on c. 2 km<sup>2</sup> in topsoil and c. 3.3 km<sup>2</sup> in bottom soil. Natural critically polluted area is located on surrounding hills, outside from the urban zone and main share in total natural pollution is principally with Ni and Cr. Anthropogenic pollution that associate high concentrations of As, Cd, Cu, Hg, Pb and Zn, exceed critical level on c. 2 km<sup>2</sup> in both soil horizons. For the mentioned association is significant that polluted area is situated in the Zenica basin and area among the river. Critically polluted area is mainly situated on the Miocene coal layers on the NW side of the study area and refers to As distribution.

#### STAVNJA VALLEY (BOSNIA AND HERZEGOVINA)

Vareš is situated in the valley of the river Stavnja with 20 000 inhabitants. In this region, iron ore mined and smelted from Antique period but with arrival Austrians to Bosnia, Vareš admire revival in economy aspect. Construction of the ironworks and metal foundry in Vareš started in 1891, and until 1991. Three Fe ore deposits Smreka, Droškovac, and Brezik are situated in municipality of Vareš. Open pit's reserves and resources in the mentioned three Fe ore deposits

are approximately 169 million tones, in 1991. Apart the Fe in hematite and siderite there are present another oligoelements such as Cu, Pb, Zn, As, Sb and Sn.

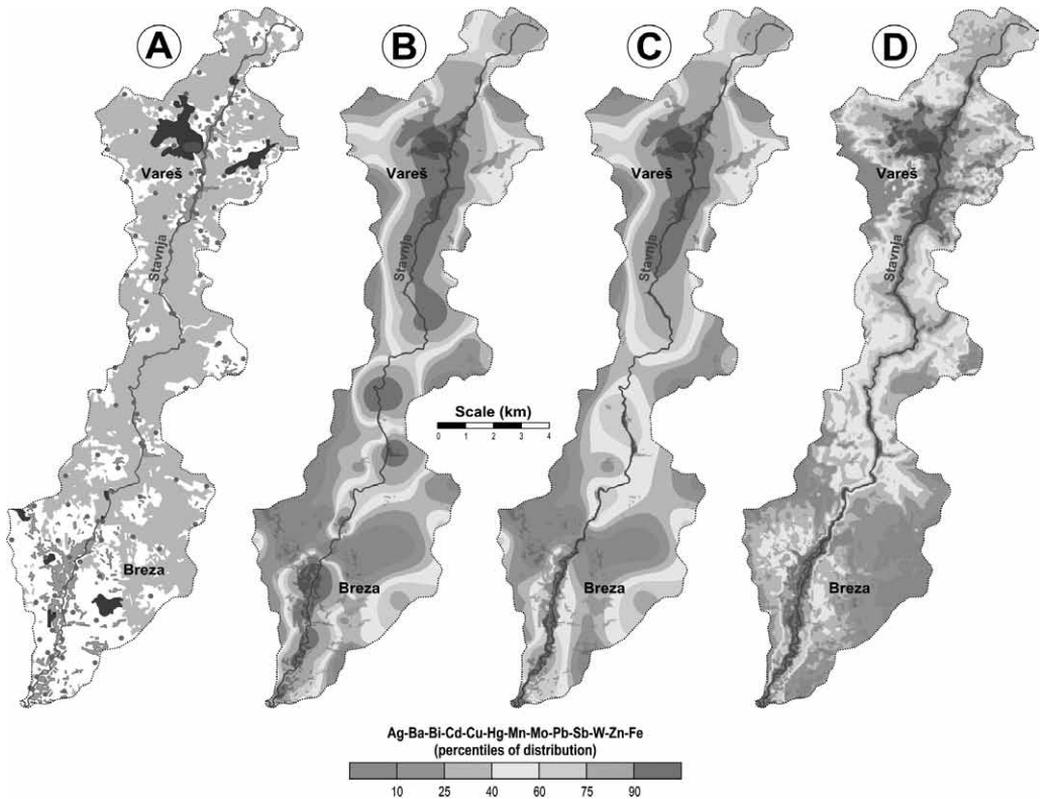
Lead, zinc and barite Veovača open pit is situated about 10 km of the town. Sulphide mineralization is associated with layers of barite and have volcanogenic – sedimentary genesis. Pb – Zn mineralization is associated with Droškovac Fe deposits. From the abandoned open pit and waste deposit “Veovača” is significant leeching of trace elements that have great influence on environmental pollution around the open pit and along the river Stavnja.

The main goals of the study have been: Identification of optimal methodology for geochemical research in the areas of former military operations (with remain minefields and/or suspected mined areas), according to the sampling material, sampling density, data processing and interpretation of results; Determination of concentration levels and spatial distribution of chemical elements in the secondary materials (soil, river sediments and attic dust) along the Stavnja valley; Assessment of the natural background according to lithology and the proportion of influence of mining and metallurgy activities on distribution of chemical elements in the secondary materials (soil, river sediments and

attic dust) along the Stavnja valley; Identification of main geochemical associations and their spatial distribution using multivariate statistical approach (PCA) and Artificial Neural Network (ANN); Design models of heavy metal dispersion around the major emitters, using multivariate statistical approach (PCA) and Artificial Neural Network – ANN (Figure 4).

At 153 sampling locations, 265 samples of soil, stream sediment and attic dust were collected. Analysis of 36 chemical elements was performed. One anthropogenic and four geogenic geochemical associations were establish on the basis of visually indicated similarity of geographic distribution of elemental patterns in the topsoil and subsoil; comparisons of basic statistics, correlation coefficient matrices; results of cluster and factor analyses and comparisons of enrichment ratios (ALIJAGIĆ & ŠAJN, unpublished data).

The geogenic geochemical associations (Cr, Ni, Co, Fe, V, Sc and Cu), (Th, La, As, K, Sc and Tl), (Al, Ga and V) and (K and P) are influenced mainly by lithology, but anthropogenic geochemical association (Pb, Zn, Ag, Sb, Hg, Cd, W, Bi, U, Mo, Mn, Ba, Sr, Ca, Cu, Tl, Fe and As) links elements that are result of historical activities of the ironworks Vareš, mining activities as well as other anthropogenic influences of metallurgical



**Figure 4.** A – Landuse map with the sampling grid (Vareš, B&H); B - spatial distribution of Ag, Ba, Bi, Cd, Cu, Hg, Mn, Mo, Pb, Sb, W, Zn and Fe using standard kriging method; C – using segment (multiple) kriging; D – using ANN (multilayer perceptron neural networks)

factors in the past. The main polluted zones are found in the city Vareš and their surroundings, where are located two Fe open pits and the Veovača, Pb-Zn-Ba mine and ironworks. Another zone with high concentration of aforementioned heavy metals has been found downstream of the river Stavnja, in alluvial sediments suitable for agricultural activities (ALIJAGIĆ & ŠAJN, unpublished data).

#### INVESTIGATION IN MACEDONIA

Cooperation GeoZS with Macedonia is basically the strongest one at the moment, which can be proved by many already published materials. We focused our geochemical researches to most polluted locations such as the mines (Cu Bučim, Pb-Zn SASA and Toranica, As-Sb-Tl Alšar), Pb-Zn smelter Veles; FeNi – Kavadarci; thermoelec-

tric power plants (Kičevo and Bitola), alluvial deposits of the Vardar river, Skopje. Here we want to present several study cases (Veles, Kavadarci and Bučim) but several other very interesting studies are: identification of heavy metals in honey samples (STANKOVSKA et al., 2007; 2008), and moss samples (BARANDOVSKI et al., 2012) in R. Macedonia; determination of chemical composition of soil around the thermoelectric plant Oslomej, in Kičevo (STAFILOV et al., 2011).

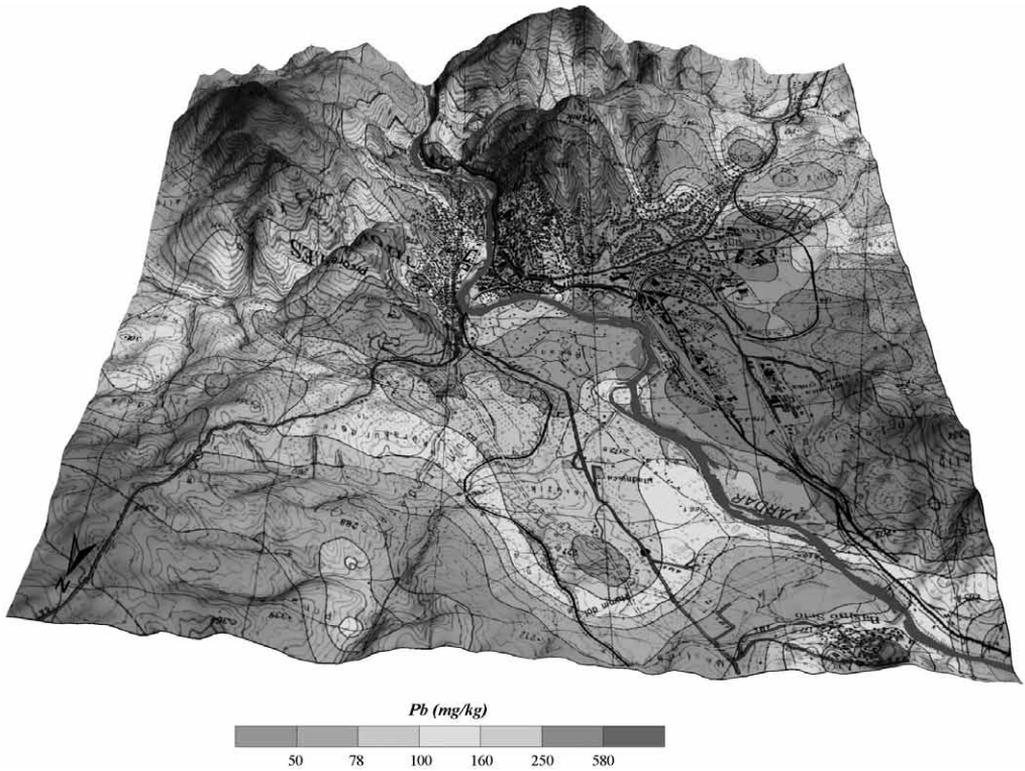
### **Veles (Macedonia)**

Veles (50 000 inhabitants) is the most polluted city in Macedonia. In the centre of town lead and zinc smelter located. The Macedonian Institute for Health Protection reported in 2003, when the factory still operated, that Veles was absorbing 62 000 t of zinc, 47 300 t of lead and 120 000 t of sulphur dioxide annually. Plans for the cleanup include ridding the city of heavy metals and decontaminating soil in the 45 ha area around the smelter.

As, Cd, Cu, Hg, In, Pb, Sb and Zn are chemical elements introduced into the environment through anthropogenic activities. Typical for this elemental assemblage is the enrichment of the elements in topsoil versus European topsoil, from 2.2-times for the Sb to 27-times for the Cd. High concentrations and as well the enrichments of mentioned elements, especially Cd in

topsoil is noticeable close to Zn smelter in Veles and in urban zone. In area of the main polluted area average concentration of Cd exceed European Cd average more than 110-times!

The shape of the dispersion halo has been strongly influenced by local winds and the shape of the Veles basin. Cd average in topsoil for the all study area amount 7.7 mg/kg in range 0.30–600 mg/kg. Considering land use, the average of Cd in cultivable area amount to 6.1 mg/kg, in uncultivable area 4.8 mg/kg, in urban area 12 mg/kg and in main polluted area 32 mg/kg. The most of highest values is in the industrial part of the region with the maximal Cd content from 76 mg/kg to 600 mg/kg, and in the part of the city which is close to the smelter plant (104 mg/kg and 105 mg/kg). In this region several topsoil samples with extremely high content of cadmium are present 420 mg/kg (3500-times higher that European topsoil average. According to experimental results, the area critically polluted with Cd is about 6.6 km<sup>2</sup>, with Pb 4.2 km<sup>2</sup> and Zn 3.8 km<sup>2</sup>. Materials for the study case are collected from the following articles: STAFILOV et al., 2008; Stafilov et al., 2010. Radionuclides in soil were studied in DIMOVSKA et al., 2010a. This work has awarded with The State Prize of the Government of Republic of Macedonia »Goce Delčev« for the scientific achievement in 2008.

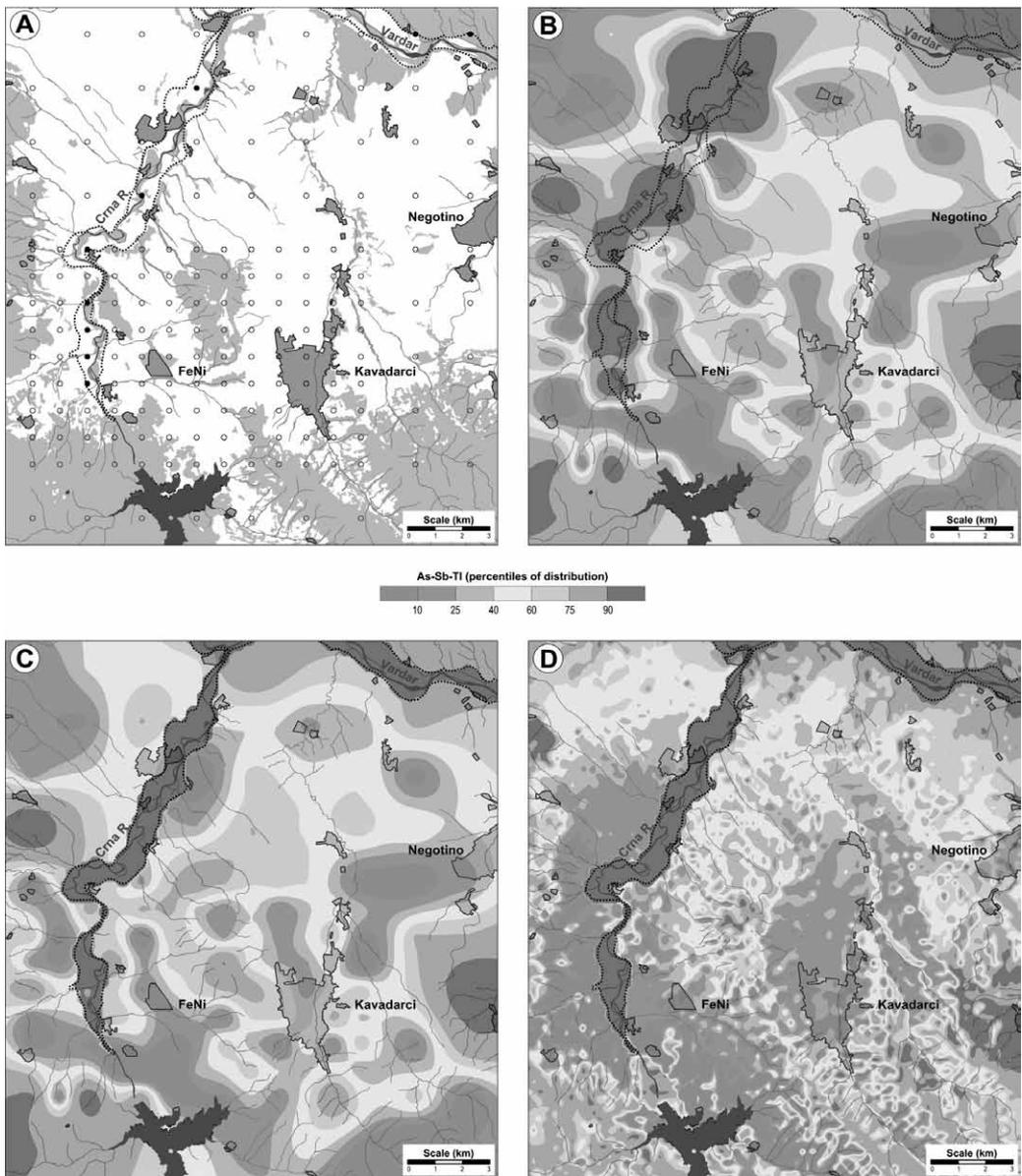


**Figure 5.** Spatial distribution of lead in topsoil (Veles, Macedonia)

### **Kavadarci (Macedonia)**

Materials for the study case are collected from the following articles: STAFILOV et al., 2008b; 2009a; 2009b; 2010b. But also several other interesting studies in this area are: BAČEVA et al., 2009; 2011; 2012a; 2012b concern atmospheric pollution; DIMOVSKA et al., 2012b represent radioactivity in soil; ŽIBRET et al., 2012 applied artificial neural network in determination of contamination; STAFILOV et al., 2012 provide an interesting study of As-Sb-Tl in this region.

Town Kavadarci is located in Tikveš valley, about 100 km south from the capital Skopje (Figure 1). The city is well known and famous by its vineyards and it is main vine production region in Macedonia. The urban area is located on 200–300 m altitude, surrounded with hills from east and south sides of the valley (with height difference between 300 m and 770 m). The climate in Kavadarci is of a continental type of climate with a reduced Mediterranean climate and with hot summer and cold winter. The major wind direc-



**Figure 6.** A – Landuse map of Kavadarci area with the sampling grid (Kavadarci, Macedonia) B – spatial distribution of As-Sb-Tl using standard kriging method; C – using segment (multiple) kriging; D – using ANN (radial basis function neural networks)

tion is from the north and northwest. The complete investigated region (360 km<sup>2</sup>) was covered by 172 sampling location. 344 soil samples of topsoil and subsoil were collected.

The highest concentrations of Cr and Ni are located on the outcropping Paleozoic serpentinites (inner parts of the Vardar zone). High, sometimes critically content of Cr and Ni in the zone of Eocene flysch is already proven in numerous researches from Macedonia and other Balkan countries. The ferromanganese smelter plant "FENI", in spite of the obvious environmental pollution has not contributed significantly to the measured amount of these elements, which occur in high concentrations in the background.

High concentrations of Cd, Hg, Pb and Zn are also found on the SW and W, hilly part of the study area as a consequence of the high concentrations of heavy metals in organic material of topsoil or the long distance transportations. High concentrations of the mentioned heavy metals were also found as a result of urban activities in the city of Kavadarci, but they are very low. The highest concentrations of As, Sb and Tl are found on the Holocene alluvium of Crna Reka. Enrichment of the Holocene alluvium of the Crna Reka is consequence of natural erosion from the mine deposits (As and Sb) of Alšar on the Kožuf Mountain, but also from

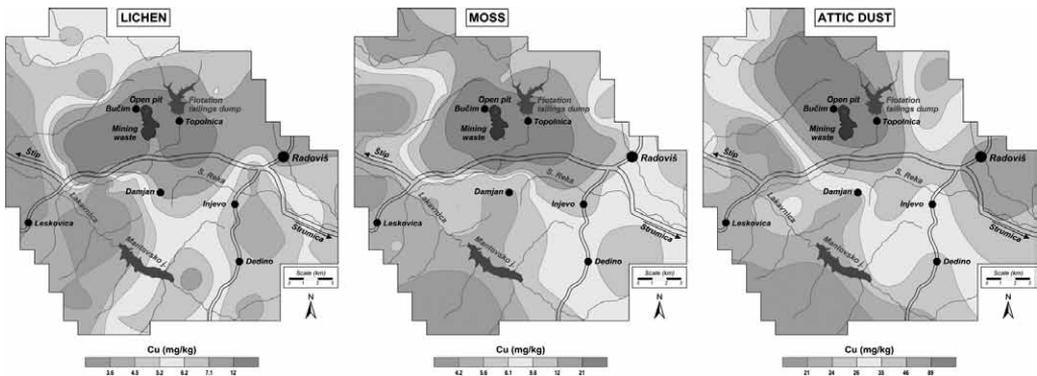
mine activities in the past. High concentrations are determined in the river sediments of Vardar River. This enrichment with As, Sb and Tl in the Holocene alluvium of the rivers Crna Reka and Vardar should be studied in the future because it is a rare example of enrichment of alluvial sediments (Fig 6). Principally, the natural enrichment is related especially to Ni. Pollution with As, Cd, Co, Cr, Cu, Hg, Mo, Pb and Zn is basically insignificant.

Construction of geochemical maps using universal kriging methods is quite useful in determination of distribution patterns, but in such a maps are present mistakes called Bull's eye effect because in the isotropic space appears elongated division, that is possible solve only with denser sampling grid. Applying the multilayer perceptron (MLP) avoiding this problem and we constructed much better maps of contamination, especially from the geological point of view (Figure 6.).

### **Bučim (Macedonia)**

Materials for the study case are collected from the following articles: BALABANOVA et al., 2009, 2010; 2011a; 2011b; 2012a; 2012b; STAFILOV et al., 2010b.

The Bučim copper mine is located in the eastern part of the Republic of Macedonia. The mine is in function from 1980 and processes 4 Mt of ore annu-



**Figure 7.** Spatial distribution of cooper in lichen, moss and attic dust (Bučim, Macedonia)

ally. The ore reserves are estimated to total about 85 Mt. The deposit is a porphyry copper type deposit and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites. The main ore body is approximately 500 m in diameter and 250 m in vertical and has been worked in a large open pit, which actually allows direct exposure of ore particles to the atmosphere. The igneous rocks have been altered into clays and micas. The basic ore proceeding process includes: drilling and blasting, than blasted ore is transported towards primary crushing while the tailings on the mine disposal.

Different sampling media: moss, epiphytic lichens and attic dust were used for comparative analysis due to monitoring air pollution and distribution of 15 elements including certain heavy metals. Thus, attic dust, moss and li-

chen have the potential for collecting complementary information on present and historical air pollution trends.

For the geogenic geochemical association Ni-Cr-Cd-Fe-Al-K-Mn-Zn is significant a similar distribution pattern, with minor variations, especially in the biogenic samples. In all observed materials, the higher concentrations are observed in the area of predominant Pliocene sediments, with fact that both patterns, in attic dust and moss are much more similar. Significant deviation from that fact represents high values in moss and lichen in the area where occur Palaeozoic rocks, mainly schist. Spatial distribution pattern of anthropogenic association As, Cu and Pb is very similar for all three sampled materials. The association presents distribution of high contents of potentially risk elements close to the anthropogenic sources.

All three treated materials are shown to be useful in determining an anthropogenic impact as well as the chemical properties or geological background on orographic diverse terrain in the presence of complex geological structure. With fact that attic dust is the most stable and responsive to environmental changes and lichen is the worst.

Based on the research results, the combinations of attic dust and moss give the best results in the determination of anthropogenic impact on the environment as well as the natural enrichment. Attic dust shows very stable historical reconstruction of contamination, moss a current state, related to a period of growth and to period of accumulation of chemical elements.

### **Kosovska Mitrovica (Kosovo)**

Materials for the study case are collected from the following articles: ALIU et al., 2009 2010; STAFILOV et al., 2020a; ŠAJN et al., 2012;

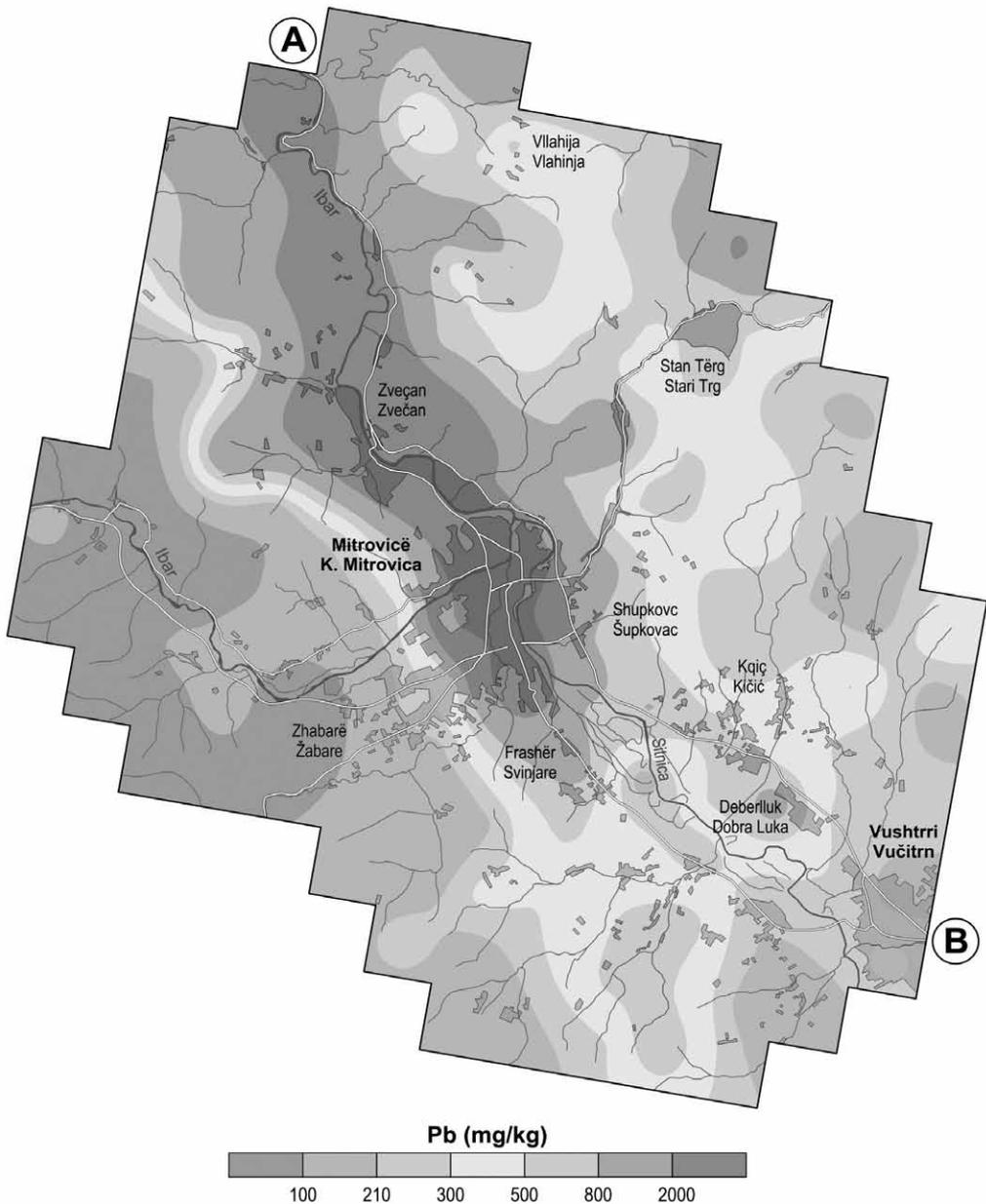
Mining and metallurgic activities in Kosovo have a long history. The Trepča Mine Limited in K. Mitrovica was built in 1927 and produced lead, arsenic and cadmium from the 1930s until 2000. The smelter close to Zvečan commenced work in 1939. Because of the smelter and three huge tailing dams, environmental pollution in K. Mitrovica increased dramatically. The smelter has been working sporadi-

cally since the 1999 conflict between Kosovo's Albanian and Serb population in Kosovo.

The total production of mine Trepča from 1931 to 1998 has been estimated at 34 350 000 t run-of-mine ore at grades of 6 % Pb and 4 % Zn. The ore was beneficiated in the flotation plants. The Pb concentrates were brought to the lead smelter of Zvečan (capacity 80 000 t per year) and the Zn concentrates were brought to the zinc smelter of K. Mitrovica (capacity 50 000 t per year); there was also a unit for the production of fertilisers and batteries. The amount of metal produced was 2 066 000 t Pb, 1 371 000 t Zn as well as Ag, Bi and Cd.

The investigated region (300 km<sup>2</sup>) was covered by a sampling grid of 1.4 km × 1.4 km. In total, 159 soil samples from 149 locations were collected. Inductively coupled plasma-mass spectrometry (ICP-MS) was applied for the determination of 36 elements. For data evaluation, parametric and non-parametric statistics methods were used.

The obtained results show that the content of Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo appeared as an anthropogenic association, which contents mainly depend on mining and processing activities. In vicinity of cities Zvečan and K. Mitrovica their content is even higher than the corresponding intervention values ac-



**Figure 8.** Spatial distribution of lead in topsoil (K. Mitrovica, Kosovo)

According to The New Dutch List exceed in 152 km<sup>2</sup> of the investigated area. The pollution is involving several extremely high elements such as Pb, Zn, Cd, Cu, Ag, and Hg. Their average contents are: Pb 450 mg/kg with a

range of 34–35 000 mg/kg, Zn 30 mg/kg in the range of 32–12000 mg/kg, Cd 1.6 mg/kg with a range of 0.10–47 mg/kg, Cu 42 mg/kg in range 9.0–1600 mg/kg, Ag 30 mg/kg in range 0.05–58 mg/kg and Hg 0.20 mg/kg in range 0.02–11 mg/kg.

There is no doubt that the mining and smelting activities left huge consequences on environment in urban zones of K. Mitrovica and Zvečan, the Trepča mines in Stari Trg, but also in alluvial sediments of the Ibar River, where intensive agriculture activities are present.

#### INVESTIGATION IN SERBIA

Geochemical researches in Serbia begun in 2011 and finish 2012, we focused our study on the alluvial sediments of river Ibar (environmental impact of mine Trepča and Pb smelter Zvečan), river sediments and river terraces of the river Timok, and the copper mine Bor where we collected the soil samples and attic dust (ŠAJN et al., 2012, unpublished data).

Bor is a town located in eastern Serbia, with one of the largest copper mines in Europe. The population of municipality has about 50 000. Basic economic activities in Bor are copper mining and metallurgy. The mine was opened in 1903 and 1905 started the

copper-smelting work. The factory, in which is now melting the copper concentrate was built from 1961 to 1968. Every year, it emits 4.86 kg to 7.99 kg of zinc, 6.27 kg to 25.11 kg of lead and 5.3 kg to 19.6 kg of arsenic per capita, which depends on the emission volume of production and content of these metals in raw materials.

Bor and surrounding is cover by 96 soil sampling sites (topsoil and bottom soil), 10 sites of urban soil and 86 sites of attic dust. First, preliminary results show that the mining and metallurgical activities in Bor and its surroundings caused numerous environmental problems, and left catastrophic consequences for the entire environment.

The river Timok with its tributaries represents a drainage water system from the copper mine Krivelj (Bor), and heavy metal industry in Bor. Hazardous waste is transported by this river to the Danube, consequently polluted by heavy metals. Sampling grid is constructed on the way that we cover the main polluted part from town Zaječar till its confluence with Dunav, but also a two main tributaries from the Krivelj mine. Altogether, 15 samples of river sediments and 15 soil samples from alluvial plains and 10 soil samples from river terraces were collected.

After the high concentrations of heavy metals especially Pb, Zn, Cd, Ag, Hg

and Cu were discovered in Kosovska Mitrovica and Zvečan, we decided to continue a sampling along the river till its confluence with the river Zapadna Morava. Total, 14 samples of river sediments, 14 alluvial sediments (top and bottom soil), 14 river terraces (top and bottom soil) and 4 soil samples on second river terraces (top and bottom soil).

## CONCLUSION

The major goals are strengthening an international scientific cooperation network and partnership between GeoZS and other former Yugoslav countries, improvement of material research standards, exploiting the research and technological demonstration results as well promoting the GeoZS to regional centres of excellence. The results of numerous geochemical studies of natural distribution and proportion of anthropogenic heavy metals in the environment, especially in areas of former mining and smelting in Slovenia and the region can be used as guiding principles for the future environmental remedial actions.

Specifically, the results from the entire study will complement our knowledge about a complexity of chemical compounds in the environment. Special emphasis is given to the further development of advanced data processing techniques and methods of linear and

nonlinear mathematical models, based on the application of modern mathematical analysis such as PCA (Principal Component Analysis), and ANN (Artificial Neural Network) at the distribution and transport of heavy metals in the environment.

Soil is together with water and air, one of the most important natural resource of country. Apart of food production, soil is a natural filter for hazardous and noxious substances that can run out to system of drinkable water and groundwater respectively. Because of that soil care, as natural treasure, represent very important priority in environmental protection. For better soil treatment, is necessary to know all soil characteristic, their concentration of chemicals and concentration of potential toxic elements as well.

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