



ANTHROPOGENIC SOIL CONTAMINATION CONNECTED WITH ACTIVE MINES, SMELTING AND PLANTS IN THE REPUBLIC OF MACEDONIA



Todor SERAFIMOVSKI¹; Goran TASEV¹; and Violeta STEFANOVA¹

¹ Faculty of Natural and Technical Sciences, University "Goce Delchev"-Štip, R. Macedonia

Introduction

The aim of this study was to quantify the chemistry of soil in the important mining and mine products processing areas in order to assess the environmental impacts of current and past mining activities (Figure 1). As major polluted localities, confirmed even with our latest results, are the areas around the open pit and cement plant Usje located in the capital Skopje, former Pb-Zn smelting plant near the Veles city limits, active ferro-nickel plant located in the well known wine region of Kavadarci, active Pb-Zn mines with their respective tailing dams in Eastern Macedonia (Toranica, Sasa and Zletovo) and active open pit of the Buchim copper mine with large waste dump and tailing dam.

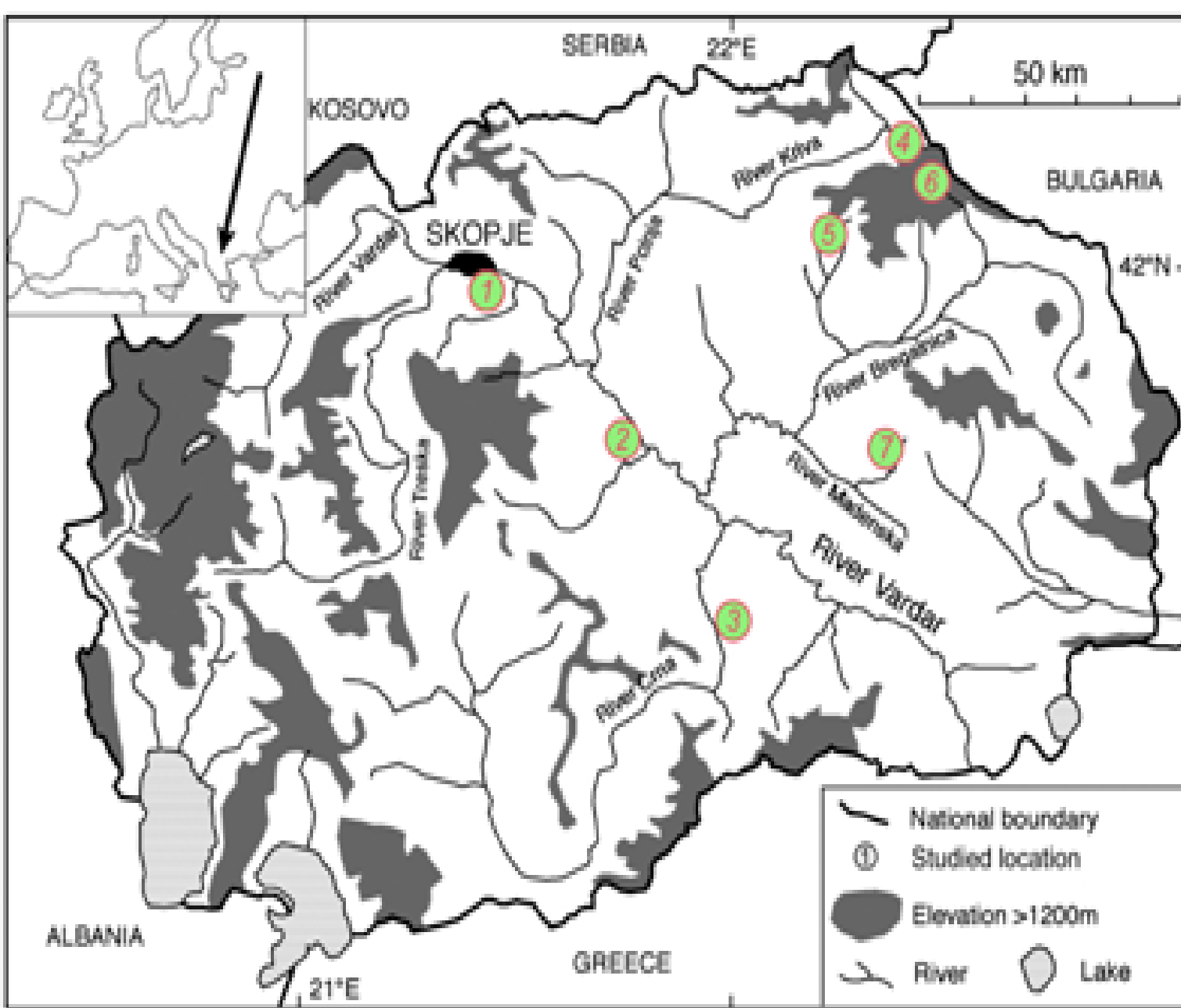


Fig. 1. Studied locations of anthropogenic pollution

1. Usje cement plant, Skopje;
2. Former Pb-Zn smelting plant, Veles;
3. FENI smelting plant, Kavadarci;
4. Toranica Pb-Zn mine, Kriva Palanka;
5. Zletovo Pb-Zn mine, Probitip;
6. Sasa Pb-Zn mine, M. Kamenica;
7. Buchim Cu mine, Radovis

Materials and Methods

Sampling was carried out over period 2005-2014. Each sample represented the composite material collected at the central sampling point itself together with at least four points collected around a central one with a radius of 1 m towards N, E, S and W directions. Analyses were conducted using emission spectrometry with inductively coupled plasma (ICP-AES) after Aqua Regia Digestion. All samples and geological standards were submitted to the laboratory in a random order assuring an unbiased treatment of samples, random distribution of the possible drift of analytical conditions for all samples and the precision was less than 5%.

Results and discussion

The Usje cement plant: Total of 15 specimens were analyzed, values ranged 1.46÷2.23% Fe, 440÷940 mg·kg⁻¹ Mn, 93.4÷104.71mg·kg⁻¹ Ni, 58.57÷83.1mg · kg⁻¹Zn, 23.1÷34.9 mg · kg⁻¹ Pb, 42.30÷60.3 mg·kg⁻¹ Cu and 0.59÷1.61 mg·kg⁻¹Cd. Calculated enrichment ratios ranged from low 0.98 for Fe, 1.4865 for Zn, 1.89 for Mn and 1.8975 for Pb, through 3.016 for Cu up to higher 5.92 for Cd and 7.5098 for Ni.

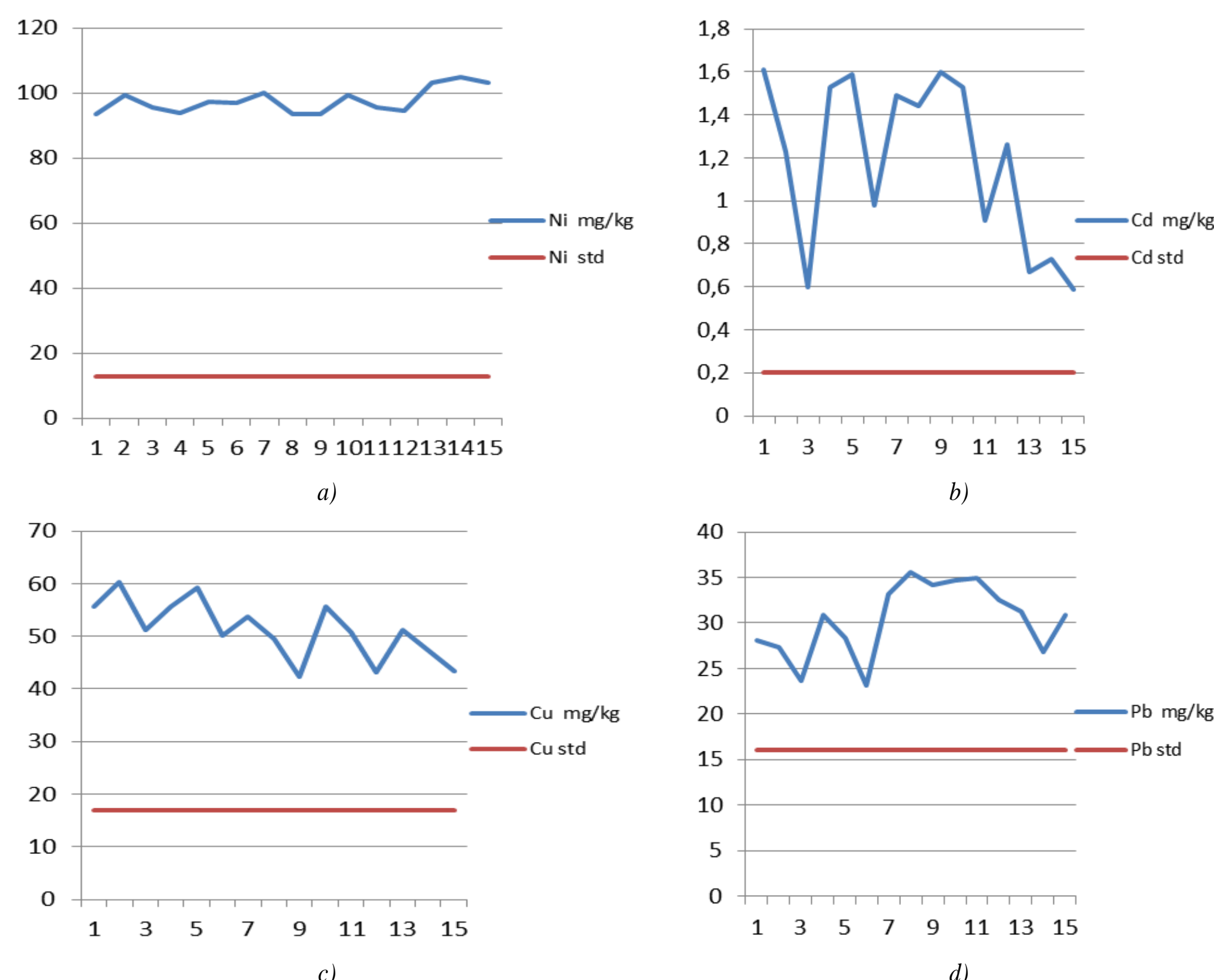
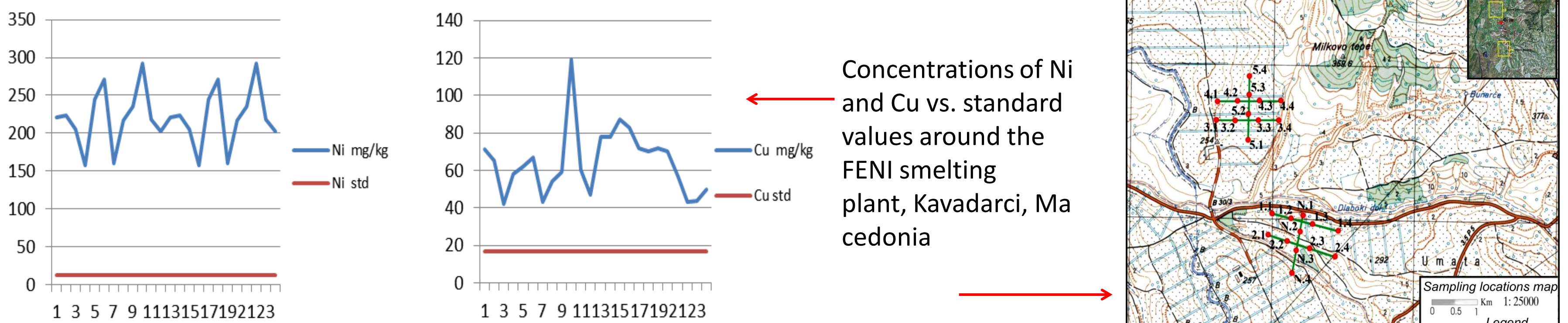


Fig. 2. Concentrations of some heavy metals vs. standard values around the Usje cement production plant, Skopje, Macedonia

The FENI smelting plant:

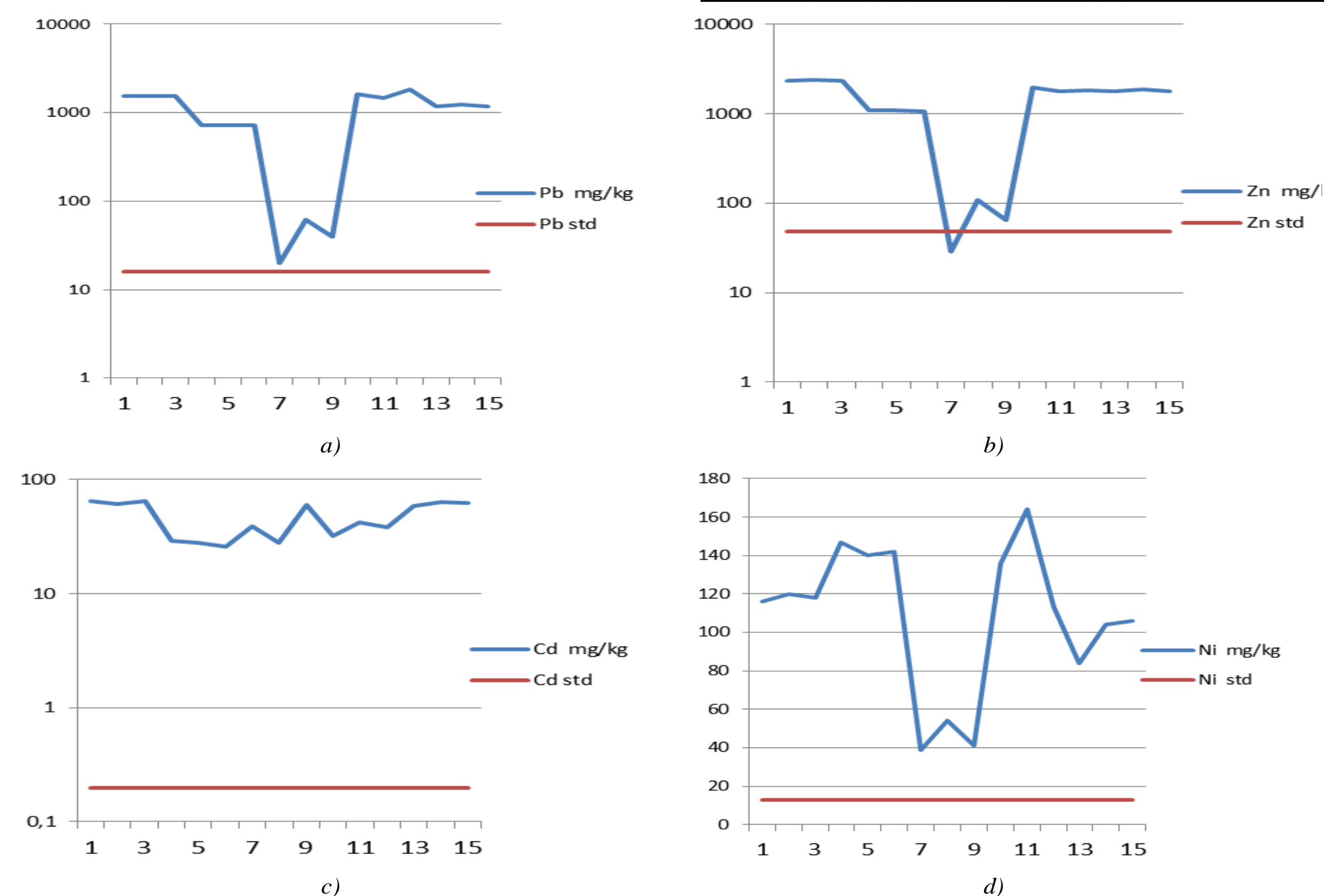
The concentrations of particular elements ranged: 16÷31 mg·kg⁻¹Pb, 117÷286 mg·kg⁻¹Zn, 13÷30 mg·kg⁻¹Co, 43÷119 mg·kg⁻¹ Cu, 158÷292 mg·kg⁻¹Ni, 519÷903 mg·kg⁻¹Mn, 119÷236 mg·kg⁻¹ Cr and 2.24÷3.79% Fe. All of them were significantly above the reference values. Enrichment ratios ranged from relatively low 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. The concentrations are increased without doubts, but findings of some other authors suggested that they cannot be attributed solely to the anthropogenic input.



The Veles smelting plant:

Concentrations of heavy metals were in the range as follows: 20÷1823 mg·kg⁻¹Pb, 29÷2395 mg·kg⁻¹Zn, 28÷65 mg·kg⁻¹Cd, 27÷81 mg·kg⁻¹ Cu, 39÷164 mg·kg⁻¹Ni, 508÷938 mg·kg⁻¹Mn and 1.6÷3.8% Fe. **All of them were significantly above the reference values.**

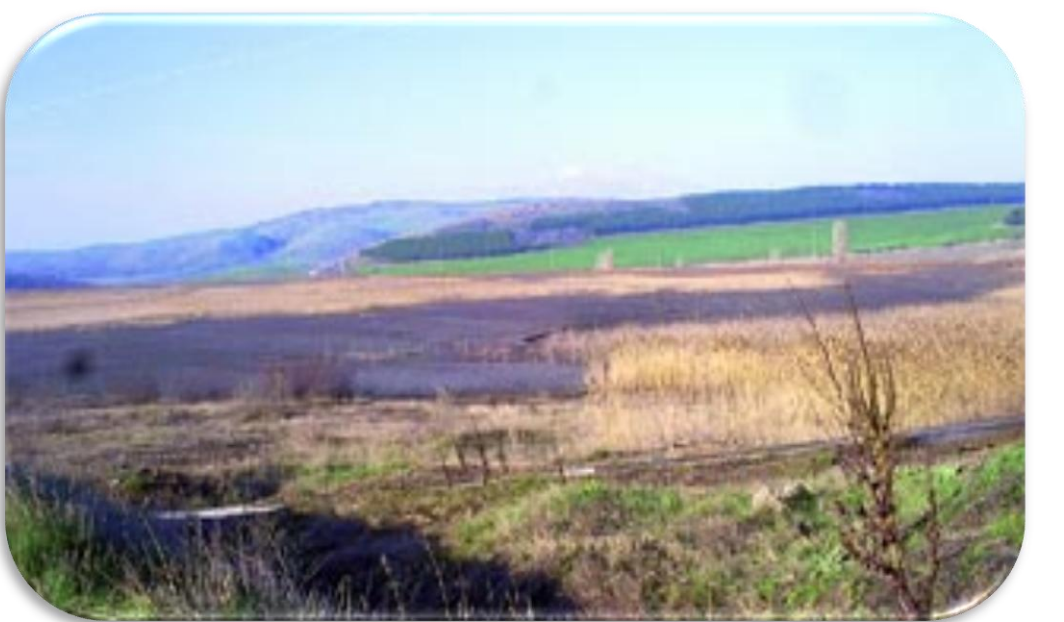
Enrichment ratios ranged from relatively low 1.67 for Fe, 2.41 for Mn and 3.27 for Cu, through the medium 8.33 for Ni and 29.95 for Zn up to high 64.05 for Pb and the highest 237.67 for Cd.



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

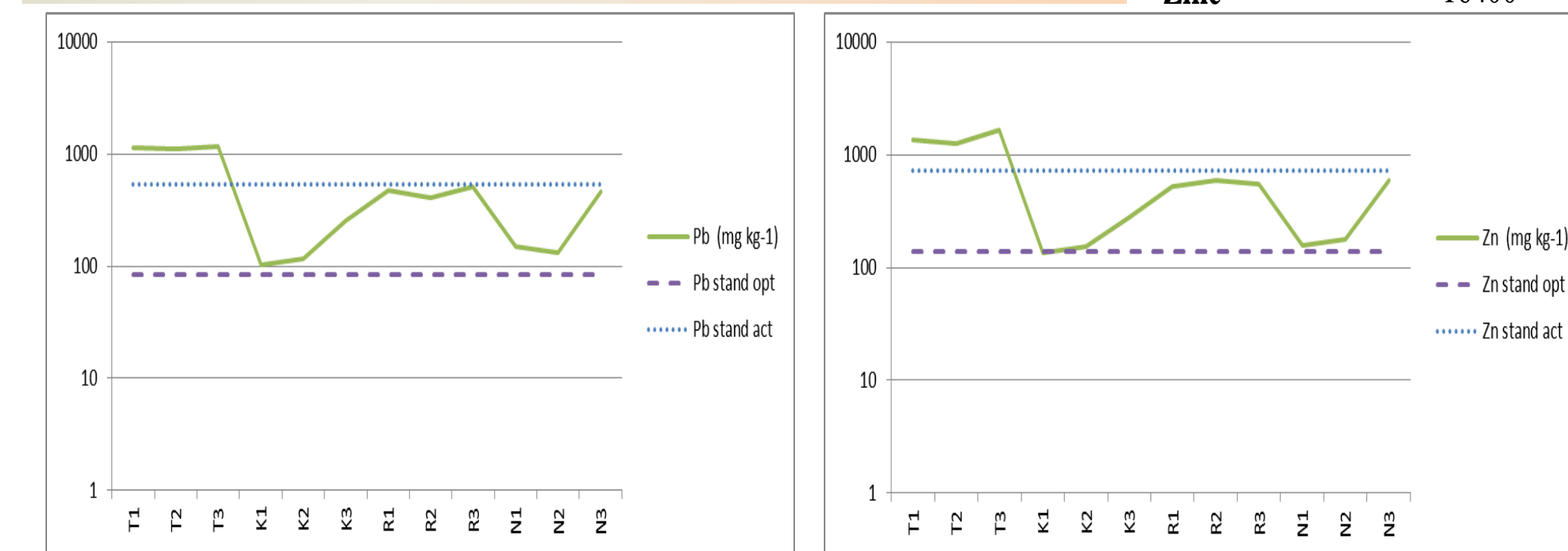
The Toranica Pb-Zn Deposit:

During the crushing and grinding of ore is released significant amount of dust. Analyses have shown that heavy metal concentrations in the dust are multiplexed above the standard values. Enrichment factors ranged from relatively low 3.75 for nickel up to 362.5 for zinc and extreme 1587.5 for lead.



The Zletovo Pb-Zn Deposit:

Airborne dust measured values multiplexed above the standard values with an exception of nickel. Enrichment factors ranged from moderate ones such were those for Cu of 20.8, Cd of 28.7, As of 32.5 up to high ones for Zn of 341.7 and Pb 925, posing very serious threat to the adjacent environment.

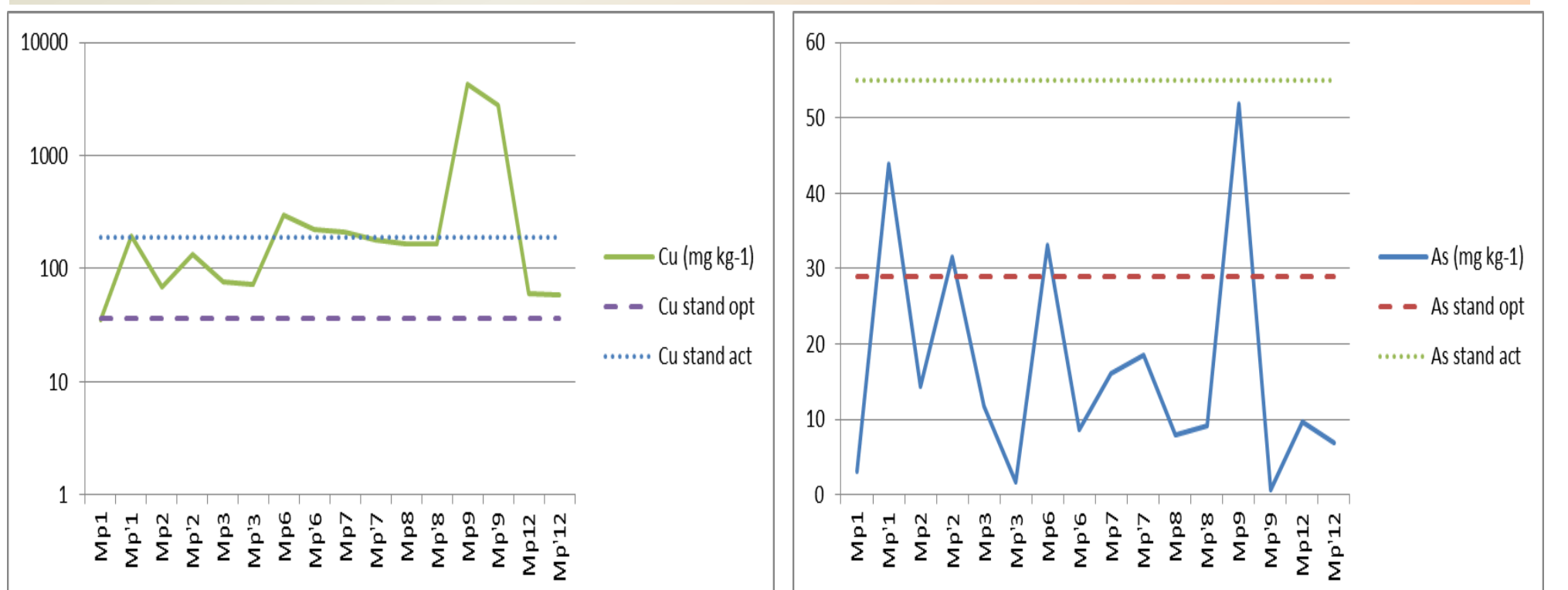


The re-sults of soil analysis around the Pisica village in the heart of Zletovo mine area reflect more realistic situation at that part of the area.

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

The Sasa Pb-Zn Deposit:

Analyses of heavy metal concentrations have shown values multiplexed above the standard values with an exception of nickel. Enrichment factors ranged from low ones, manganese of 12.14 and arsenic of 15.72, median for copper of 59.15, high for cadmium of 126 and extremely high for zinc with 892.7 and lead 1201.9. Increased concentration of heavy metals introduced by deposition from airborne dust and potential dispersion by wind activity, without any doubts poses very serious threat to the adjacent environment



The Buchim Cu Deposit:

We have followed the sampling and analysis programme as for lead-zinc mines. From the copper plot can be seen that in all the samples it was above optimal reference values and majority of them were above the action reference values, too. The arsenic have several samples with concentration above optimal reference values and none above the action reference value.

Conclusion

The results of this study have shown that at all the localities are characterize by increased values of pollutant heavy metals in soil, which can be attributed to the anthropogenic influx around the aforementioned mines and mine related processing facilities. Pollution halo diameter around them sometimes reaches over 20 km, especially in stream sediments along active water flows (ex. Toranica and Sasa). Along common pollutants (Pb, Zn, Cd) at lead-zinc and Veles smelting were determined increased concentrations of As, Ag, W, Ni, Co etc., while around the FENI smelting along to Fe and Ni were determined increased values of Cr, V, Co, Mn etc.