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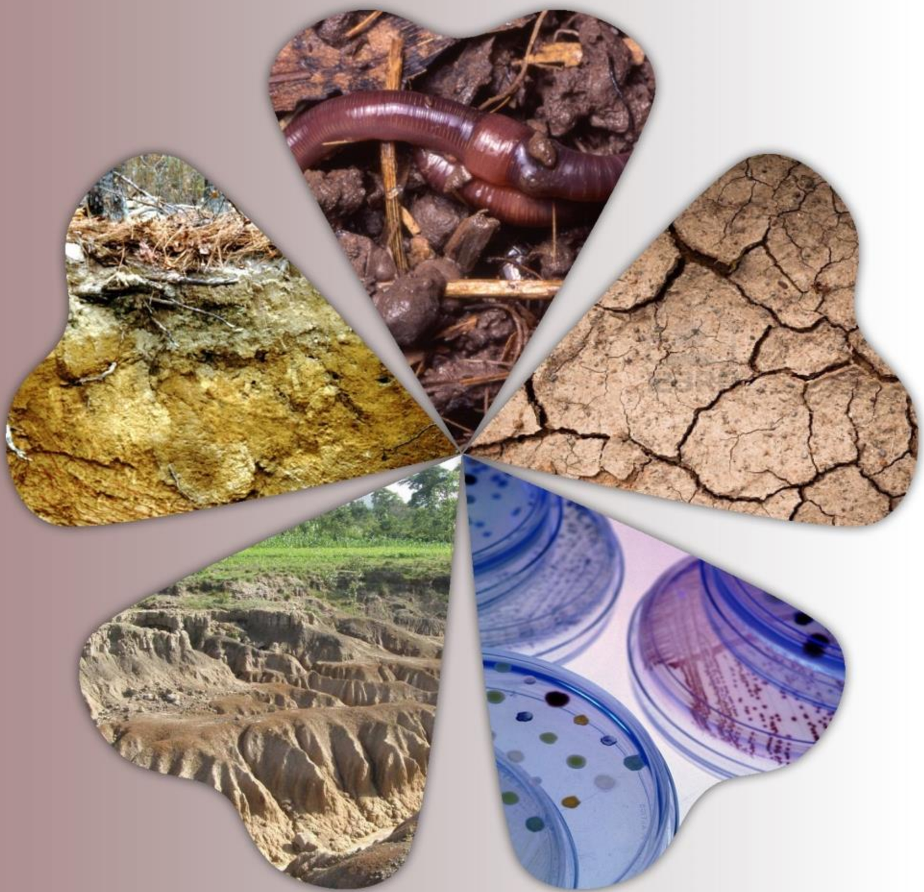

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Anthropoghenic soil contamination connected with active mines, smelting and plants in the Republic of Macedonia

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Abstract

A few anthropogenic pollutants at the territory of the Republic of Macedonia, were studied, three Pb-Zn mines with three mills, one copper mine with mill and copper leaching facility, one Pb-Zn smelting and several mines and factories for raw minerals such is the Usje in our capital Skopje. At the Usje factory were measured values in ranges of 1.46÷2.23% Fe, 440÷940 mg kg^{-1} Mn, 93.4÷104.71mg kg^{-1}Ni, 58.57÷83.1 mg kg^{-1}Zn, 23.1÷34.9 $mgkg^{-1}$ Pb, 42.30÷60.3 mg kg^{-1} Cu and 0.59÷1.61 $mgkg^{-1}$Cd. The concentrations of heavy metals at Veles former smelting Pb-Zn plant were in the range: 20÷1823 mg kg^{-1}Pb, 29÷2395 mg kg^{-1}Zn, 28÷65 $mgkg^{-1}$Cd, 27÷81 mg kg^{-1} Cu, 39÷164 mg kg^{-1}Ni, 508÷938 $mgkg^{-1}$Mn and 1.6÷3.8% Fe, all of them above reference values. Around the Feni smelting plant concentrations of particular pollution elements were in the range: 16÷31 mg kg^{-1}Pb, 117÷286 $mgkg^{-1}$Zn, 13÷30 mg kg^{-1}Co, 43÷119 mg kg^{-1} Cu, 158÷292 mg kg^{-1}Ni, 519÷903 $mgkg^{-1}$Mn, 119÷236 mg kg^{-1} Cr and 2.24÷3.79% Fe. At the ToranicaPb-Zn mine all the measured values multiplexed above the standard values. Enrichment factors ranged from, low 3.75 for nickel up to 362.5 for zinc and extreme 1587.5 for lead. The Zletovo Pb-Zn mine has been characterized by all the measured values multiplexed above the standard values with an exception of nickel. Enrichment factors ranged from mediate ones such were those for copper of 20.8, cadmium of 28.7, arsenic of 32.5 up to high ones for zinc with 341.7 and lead 925. In regards to SasaPb-Zn mine all the measured values multiplexed above the standard values with an exception of nickel. Enrichment factors ranged from low for 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. In regards to the Bucim copper mine the median values for Cu in samples were 396 mg kg^{-1} and the ranges from 94.8 to 1171 mg kg^{-1}, for the Topolnica village the median values in samples were 150 mg kg^{-1} with ranges from 52.5 to 1183 mg kg^{-1} and for the Bučim village the median values were 145 mg kg^{-1} and the ranges from 85.3 to 317 mg kg^{-1}.

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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 urban part of the capital Skopje, former Pb-Zn smelting plant located at the Veles city limits, active ferro-nickel plant located in the well known wine region of Kavadarci, active lead and zinc 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.

Preventative measures are a must where mine and mine related plant are processing and produce significant environmental influx, so understanding the environmental impact of these processes is crucial. Metal mining

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has traditionally been an important part of the economy of the Republic of Macedonia and recently increased in importance due to governmental efforts to stimulate mining through renewed exploration and development, though the country relies on its agriculture and must safeguard its soil and water resources. Pollution from current and past mine and mine related processing represents a significant problem in several parts of the Republic of Macedonia. This problem continuously is solved at active mines and mine related processing plants while the solution of this particular problem is harder to solve at mines or plants with ceased production such is the Veles former Pb-Zn smelting plant. This paper presents the latest findings related to soil pollution at all above mentioned localities followed by respective interpretation.

Material and Methods

Sampling was carried out over a prolonged period of time (2005-2014). Soil surface samples (0 cm to 5 cm depth) were collected from several localities pointed earlier as potential so-called "hot spots" in regards to heavy metal pollution (Figure 1). Samples were located using the Global Positioning System (GPS), topographic maps at scale of 1:25 000 and Google Earth maps (http://earth.google.com/). 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.

The composite material of each sample (about 0.5 kg) was placed into plastic self-closing bags and brought to the Faculty of Natural and Technical Sciences, University "Goce Delcev" Stip, Republic of Macedonia, where they were prepared for atomic spectroscopy. All of the collected soil samples (at Toranica we were forced to sample sediments due to morphology of nature) were then shipped to the Institute of Chemistry at the Faculty of Natural Sciences, University "Sts.Cyril and Methodius" Skopje, R. Macedonia. Analyses were conducted using emission spectrometry with inductively coupled plasma (ICP-AES) after Aqua Regia Digestion. All samples as well as geological standards were submitted to the laboratory in a random order. This procedure assured an unbiased treatment of samples and a random distribution of the possible drift of analytical conditions for all samples and the precision was less than 5%.

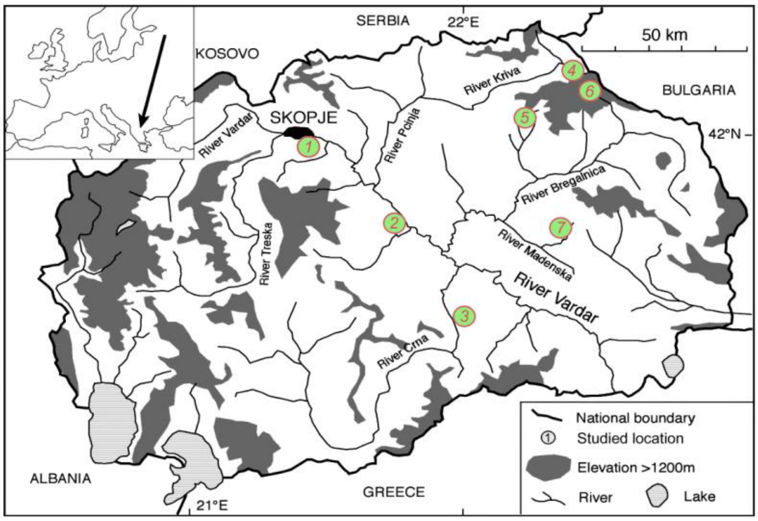


Figure 1. Studied locations of anthopoghene pollution
1. Usje cement plant, Skopje; 2. Former Pb-Zn smelting plant, Veles; 3. FENI smelting plant, Kavadarci; 4. Toranica Pb-Zn mine, Kriva Palanka; 5. Zletovo Pb-Zn mine, Probistip; 6. Sasa Pb-Zn mine, M. Kamenica; 7. Buchim Cu mine, Radovis

Results and Discussion

The Usje cement plant: 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 (Serafimovski et al., 2011a). 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 mg kg^{-1} Mn, 93.4÷104.71mg kg^{-1} Ni, 58.57÷83.1mg•kg^{-1}Zn, 23.1÷34.9 mg•kg^{-1} 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) spe-aks itself regarding the level of contamination. Calculated enrichment ratios ranged from relatively 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. Obtained results served as a basis for plots construction of particular heavy metals vs. their maximally allowed concentrations in soils (Figure 2). 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.

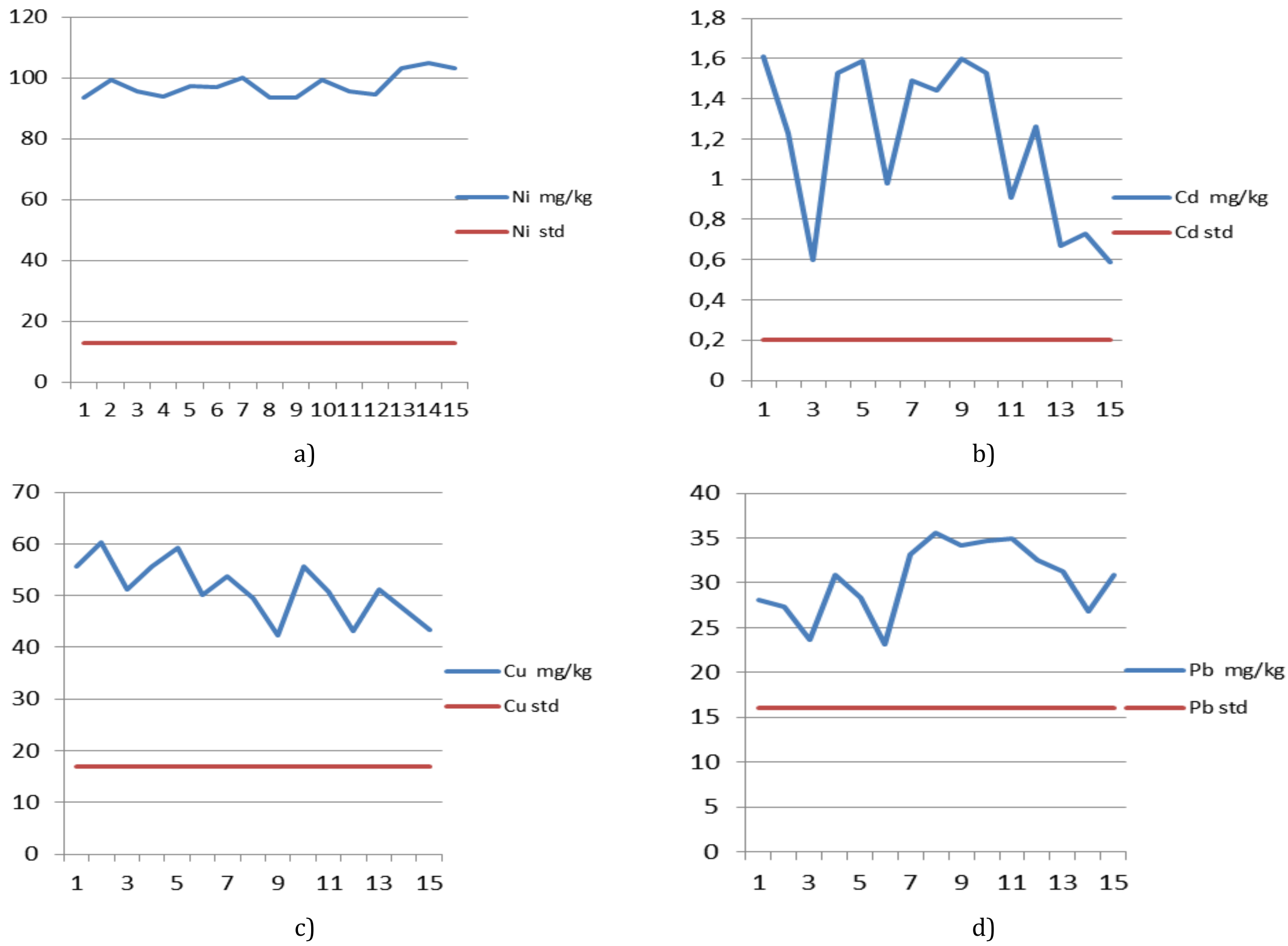


Figure 2. Measured concentrations of some heavy metals vs. standard values around the Usje cement production plant on the city limits of Skopje, Macedonia
a) Nickel; b) Cadmium; c) Copper and d) Lead

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 Veles smelting plant: This plant was the largest capacity for lead and zinc in former Yugoslavia with the capacity for producing 65 000 tons of zinc and 45 000 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 Bashino Selo, 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 3).

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 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 findings are given very illustratively on the plots at Figure 4. Also, after detailed study it was determined that values from respective sampling points were spatially dependent. Namely, as can be seen from the plots 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.

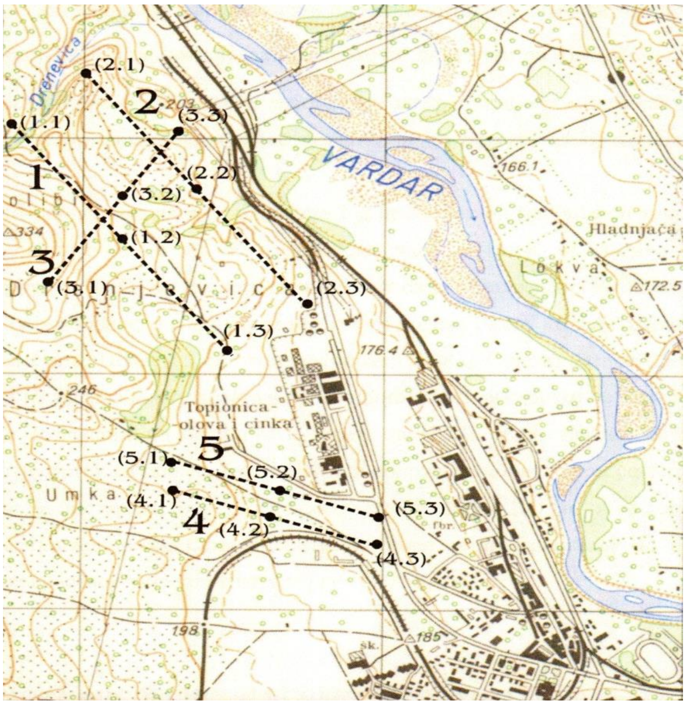


Figure 3. Spatial distribution of profile lines and sampling points along them

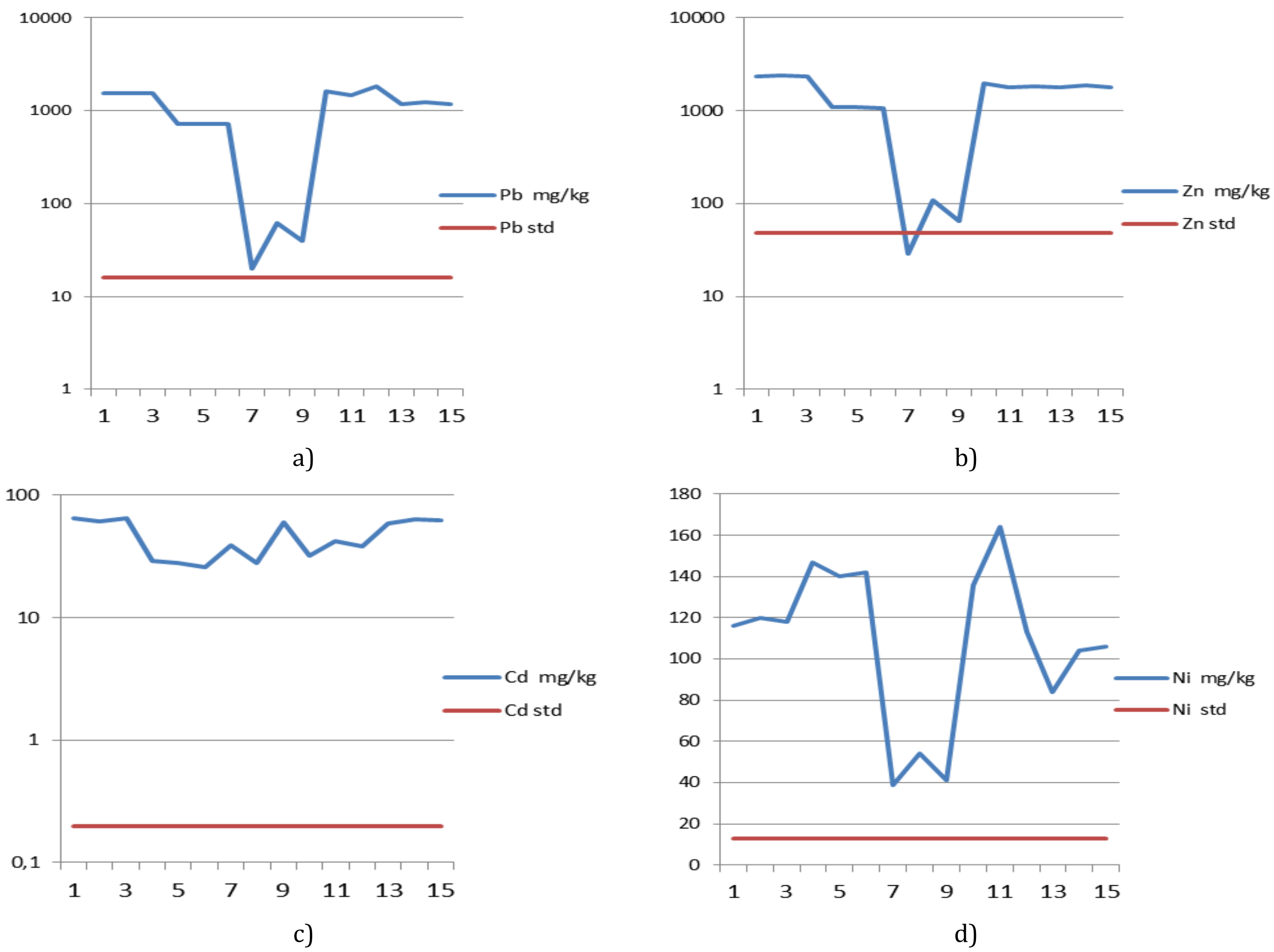


Figure 4. Measured concentrations of some heavy metals vs. standard values around the former MHKZletovo's smelting plant near the city of Veles, Macedonia

a) Lead; b) Zinc; c) Cadmium and d) Nickel (Note: Plots a, band chave logarithmic vertical scale)

Also, after detailed study it was determined that values from respective sampling points were spatially dependent. Namely, as can be seen from the plots 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 FENI smelting plant: 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 producing 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 5). 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. 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 reference values (Figure 6). 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.

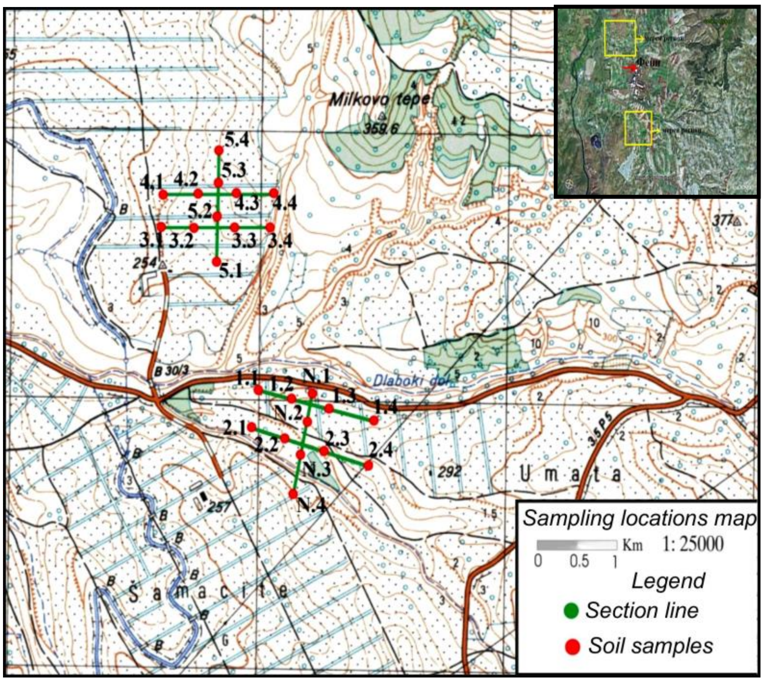
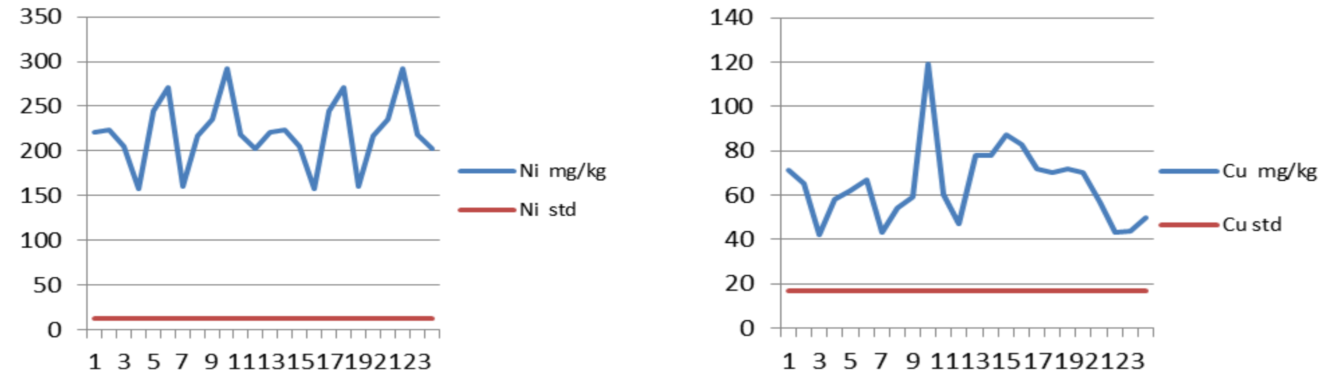


Figure 5. Sampling locations around the FENI Industries smelting plant, small inset at the right upper corner gives the satellite position of the area.



a) b)

Figure 6. Measured concentrations of some heavy metals vs. standard values around the Feni-industries'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 (Stafilov et al., 2008b, 2010; Serafimovski et al., 2011a). 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 was granted on among the first in Macedonia.

The Toranica mine area: Concerning the environmental impact of this mine, we have started our studies with analysis of airborne dust produced during the processes of crushing and grinding of ore (Walton et al., 2003a; Serafimovski et al., 2011b). During this operation was released significant amount of dust, which may pose serious threats to the environment. Analyzes have shown that heavy metal concentrations in the dust are as those given in Table 1, where can be seen that all the measured values multiplexed above the standard values. Enrichment factors ranged from relatively low 3.75 for nickel up to 362.5 for zinc and extreme 1587.5 for lead. Such high levels of concentration of heavy metals introduced by deposition from airborne dust and potential dispersion by wind activity pose very serious threat to the adjacent environment.

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

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

In the vicinity of the Toranica mine was not possible to take soil samples due to fact that the mine has been located in mountanious area (1400-1800 m) with steep canyon of the Toranicka Reka, so we have decided to sample stream sediments instead of soils (Table 2). Their analysis reflects the situation with environmental pollution as a direct consequence of the mine processing although on part of the metals have been deposited by water courses. 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 kilometers downstream. All the metals are showing increased concentrations in the sediment samples taken from the vicinity of the Toranica Mine area. After inensive result analysis there were constucted a lot of plots, comparing actual metal values certain standard values.

Table 2. Concentrations of metals in sediment samples from adits and streams in the Toranica mine area

	n	Median	Range		Dutch list standard optimal	Dutch list standard action	above standard	below standard
			min	max				
Fe (%)	11	3,86	1,41	7,9	1,8	-	10	1
Zn(mg kg^{-1})	11	8100	600	134700	140	720	11	0
Pb (mg kg^{-1})	11	14100	310	44500	85	530	11	0
Cu (mg kg^{-1})	11	802,3	68,22	7434,6	36	190	11	0
Cd (mg kg^{-1})	11	69,81	5,98	1026,8	0,8	12	11	0
Co (mg kg^{-1})	11	19,81	4,99	47,76	9	240	8	3
Ni (mg kg^{-1})	11	43,51	23,06	81,28	35	210	8	3
Ag (mg kg^{-1})	11	11,73	0,15	58,14	0,5	15	4	7
As (mg kg^{-1})	11	66,1	4,13	214,9	29	55	9	2
Cr (mg kg^{-1})	11	43,98	22,92	56,47	100	380	0	11

Sample of those increased values of Pb and Zn against standard values is given at Figure 7 and 8. Increase of measured values is especially intense in the area of taillings dam (TS10, TS11, TS12). Deposition of metals in tailling took place during the long period of time and that is why the metal concentrations in sediments are very high there.

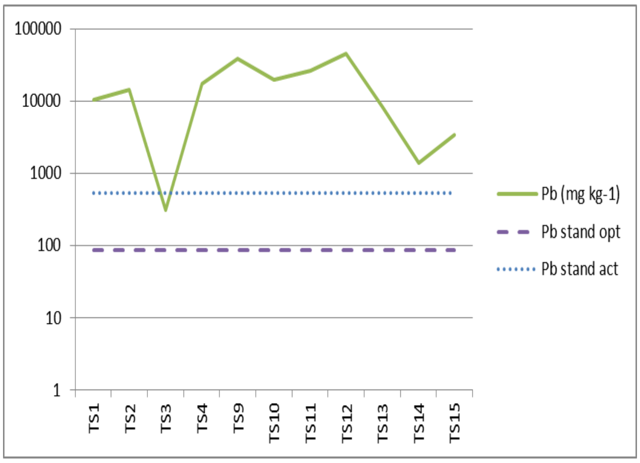


Figure 7. Diagram of lead distribution in the soil compared with optimal and action values

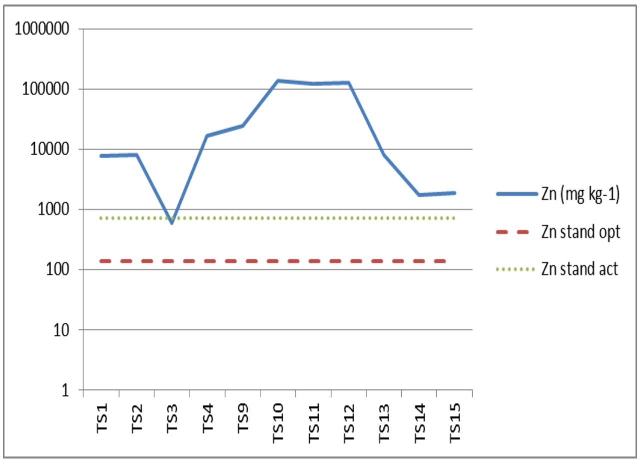


Figure 8. Diagram of zinc distribution in the soil compared with optimal and action values

The Zletovo Pb-Zn Deposit: Study of environmental impact of the Zletovo mine was in the same manner as for the previous Toranica mine. We have started with study of airborne dust produced during the processes of primary crushing of ore, since during this operation is released significant amount of dust, which pose serious threats to the environment (Walton et al., 2003b; Serafimovski et al., 2011b; Tasev and Serafimovski, 2011). Analyzes displaying heavy metal concentrations in the dust are given in Table 3.

Table 3. Analytical data of major heavy metal pollutants in the airborne dust around the primary crushing facility at Zletovo mine, Macedonia (in mg kg^{-1})

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

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

Soil sampling around the Zletovo mine have been performed by numerous researchers but without any systematics and due to such fact it was very hard to prepare one complete analysis, which would reflect real situation regarding soil pollution. In this occasion we have decided to use the results of soil analysis around the Pisica village in the heart of Zletovo mine area (Sijakova-Ivanova and Paneva-Zajkova, 2005) that reflect more realistic situation at that part of the area. The results are given statistically in Table 4, while its interpretation is illustrated at plots on the Figure 9 and 10).

Table 4. Values of macroelements and micro elements in the soils of Pisica.

			Range		Dutch standard optimal	Dutch standard action	above standard	below standard
	n	Median	*min*	*max*				
Fe (%)	12	4,21	3,87	5,11	1,8	-	12	0
Ni (mg kg^{-1})	12	19,5	16,18	22,64	35	210	0	12
Cr (mg kg^{-1})	12	26,01	22,63	29,08	100	380	0	12
Zn (mg kg^{-1})	12	538,55	134,7	1649,7	140	720	11	1
Cu (mg kg^{-1})	12	55,03	31,97	133,49	36	190	8	4
Pb (mg kg^{-1})	12	431,81	102,26	1164,8	85	530	12	0
Cd (mg kg^{-1})	12	7,88	6,44	14,51	0,8	12	12	0
Co (mg kg^{-1})	12	17,055	14,91	18,59	9	240	12	0
As (mg kg^{-1})	12	16,545	1,93	66,1	29	55	5	7
Ag mg kg^{-1})	12	0,947	0,04	3,33	0,5	15	8	4

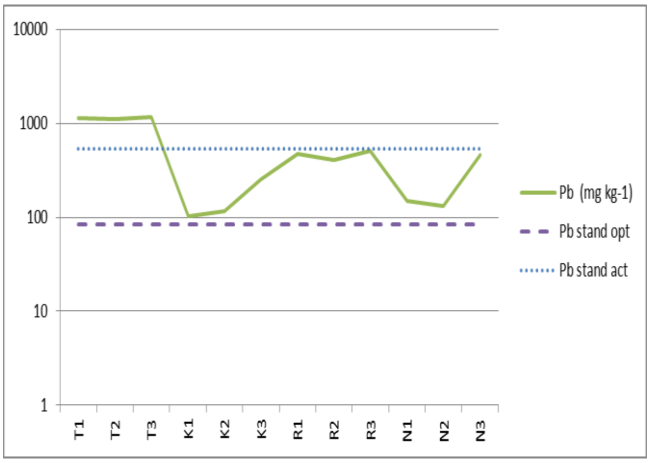


Figure 9. Diagram of lead distribution in the soil compared with optimal and action values

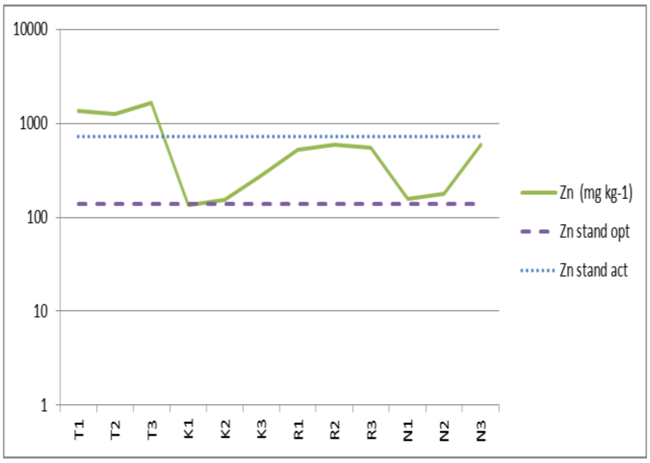


Figure 10. Diagram of zinc distribution in the soil compared with optimal and action values

Data correlation analysis found especially high correlation coefficients between certain elemental pairs: Pb-Zn 0.9869, Pb-Cd 0.9851, Pb-Cu 0.9621, Pb-Ag 0.9357, Pb-As 0.9224, Zn-Cd 0.9834, Zn-Ag 0.9220, Cu-As 0.9669, Cu-Cd 0.9466, Cu-Ag 0.9272, Ag-Cd 0.9480 etc.

The Sasa Pb-Zn Deposit: The last but not least important in the series of study of lead-zinc mines was the Sasa mine. Study of its environmental impact was in the same manner as for the previous Toranica and Zletovo mines. First of all we started with the study of airborne dust produced during the processes of primary and secondary crushing of ore, since during these operationsare released significant amounts of dust, which can lead to serious threats to the environment (Walton et al., 2003c; Serafimovski et al., 2011b). Analyzes of heavy metal concentrations in the dust are given in Table 5. As can be seen from the table all the measured values multiplexed above the standard values with an exception of nickel. Enrichment factors ranged from low ones such were those manganese of 12.14 and arsenic of 15.72, median for copper of 59.15, high for cadmium of 126 and extremely high for zinc with 892.7 and lead 1201.9.

Table 5. Analytical data of major heavy metal pollutants in the airborne dust around the primary crushing facility at Sasa mine, Macedonia (in mg kg^{-1})

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

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, being compatible with findings of Alderton et al. (2005).

The Buchim Cu Deposit: The only one active copper mine within the Macedonia joined the lead-zinc mines in our study of their environmental impact. We have followed the sampling and analysis programme as for lead-zinc mines. Considering airborne dust pollution we would like to stress out that the study on this subject already exists (Balabanova et al., 2011a, 2011b), so we used it as representative one. Also, interesting copper and other elements anomalies in soils, in the Buchim mine vicinity, were given by Stojanovska (2005) and Serafimovski et al. (2011b). The results are displayed in Table 6, while the distribution of major pollutants Cu and As are displayed at Figure 11 and 12.

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.

Table 6. Values of macroelements and micro elements in the soils of the Buchim mine vicinity.

	n	Median	Range *min*	Range *max*	Dutch Standard optimal	Dutch standard action	Above standard	Below standard
Al (%)	16	2,03	1,51	2,92	4,7	-	0	16
Fe (%)	16	3,67	2,43	5,26	1,8	-	16	0
Cu (mg kg^{-1})	16	165,19	35	4248	36	190	15	1
Ni (mg kg^{-1})	16	40,67	15,28	360,42	35	210	8	8
Cr (mg kg^{-1})	16	57,54	28,6	203,25	100	380	2	14
Zn (mg kg^{-1})	16	74,82	40,64	261,41	140	720	1	15
Pb (mg kg^{-1})	16	23,46	8,71	151,73	85	530	3	13
Co (mg kg^{-1})	16	17,08	10,24	41,82	9	240	16	0
Cd (mg kg^{-1})	16	5,01	3,15	7,08	0,8	12	16	0
V (mg kg^{-1})	16	56	38	88	42	250	15	1
As (mg kg^{-1})	16	10,66	0,7	51,92	29	55	4	12
Ag (mg kg^{-1})	16	0,405	0,16	1,01	0,5	15	4	12

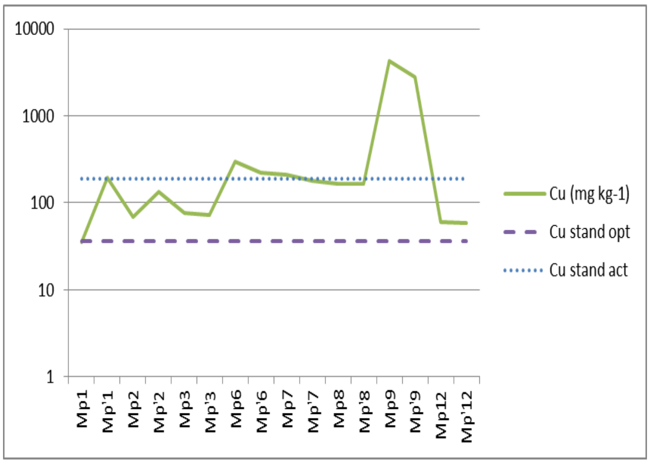


Figure 11. Diagram of copper distribution in the soil compared with optimal and action values

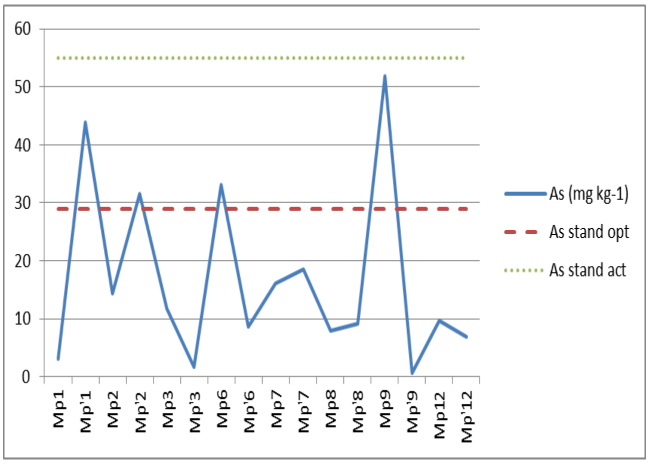


Figure 12. Diagram of arsenic distribution in the soil compared with optimal and action values

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 anthropoghenic 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.

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