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SPATIAL DISTRIBUTION OF HEAVY METALS IN THE SOILS OF BĂIUŢ AREA, MARAMUREŞ COUNTY, ROMANIA

Ioana CHIRA[1], Gheorghe DAMIAN[1,2] & Răzvan CHIRA[2]
[1]*Alexandru Ioan Cuza" University of Iaşi, Department of Geology, 20A Carol I Boulevard, 700505 Iaşi, Romania*
e-mail:yoananm29@yahoo.ccom
[2]*Tehnical University of Cluj Napoca, North University Center of Baia Mare, 62/A, Dr. Victor Babeş, Baia Mare, Romania, e-mail: damgeo@ubm.ro*

Abstract: Soil pollution is one of the key issues requiring priority resolution in a small mining area Băiuţ – Văratic. A field survey was conducted to investigate the metal contamination in soils of Băiuţ Văratec base metal mining area, near Baia Mare, northwestern Romania. Based on detailed geochemical and mineralogical analyses, carried out on soil samples, dump samples and tailing dam samples were made pollutant distribution maps. The results show high values for Cu, Pb, Cd, Zn,Ni and As. The values for heavy metals in soil are between 17.23 – 2184.1 ppm for Cu, 18.98 – 6362 ppm for Pb, 101.12 – 2834.7 ppm for Zn, 0.12-20.9 ppm for Cd, 1.52 – 311.4 ppm for Ni and between 0.004 – 266.7 ppm for As. The analysis of distribution maps for all elements clearly marked polluted areas that are close to the sources of pollution, waste dumps and tailings dams. The main environmental impact of the Văratec Băiuţ mine consists in soil contamination with heavy metals through acid mine drainage. The final results illustrated that the environment has been polluted by industrial activities.

Keywords: mining, heavy metals, spatial distribution, GIS, soil pollution,

1. INTRODUCTION

Mining sites associated with nonferrous deposits represent an important source of heavy metal pollution for soils and sediments (Alloway, 1995). Mining activities generate environmental impact, through direct and indirect effects on the environment and ecosystems, through changes which affect environmental integrity, flora, fauna, soil, air, water, climate and landscape (Siegel, 2002; Sherene, 2010).

Overall concentration of metals in the soil is determined by geological background, geochemical processes and anthropogenic sources (Bradl, 2005). The intensity of these factors varies by region, which causes a spatial variation of the heavy metal total concentration. Heavy metals natural occurrence is rocks and ores minerals (Akinmosin et al., 2009).

Heavy metals in environment may accumulate to toxic levels without visible signs. This may occur naturally from normal geological phenomenon such as ore formation, weathering of rocks and leaching or due to increased population, urbanization, industrial activities, agricultural practices, exploration and exploitation of natural resources (Ajayi & Osibanjo, 1981).

2. GEOLOGY AND SOURCES OF POLLUTION

Baia Mare was one of the most important regions in terms of the exploitation of base metal (Marias, 2005). Base metal ores are closely related to the Neogene magmatic rocks. Băiuţ ore deposit is located about 45 km east of Baia-Mare, (Fig. 1). In this ore deposit there are two mineralization areas: Breiner and Văratec (Mariaş, 2005).

The deposit is a base metal mineralization predominantly consisting of sphalerite, pyrite, galena and chalcopyrite (Borcoş et al., 1977, Gheorghiţă, 1962). The deposit was mined from the Middle Ages until 2006, resulting numerous sterile dumps the on the entire perimeter, which produced and maintain a high degree of environmental pollution, (Mariaş, 2005).

Băiuţ - Breiner mining area consists of sedimentary rocks from Jurassic, Cretaceous, Paleogene and Neogene and of post-tectonics sedimentary deposit, intrusive Neogene rocks, hornfels and cataclastics rocks. Predominant sedimentary rocks are the Paleogene, belonging to Tocila-Secu flysch (Bombiţă, 1972), which consists mainly of rhythmic deposition of clay, silt intercalated with sandstones. Upper Cretaceous and Paleogene Formations are included in Botiza Nape system of Transcarpathian flysch, (Bombiţă, 1972).

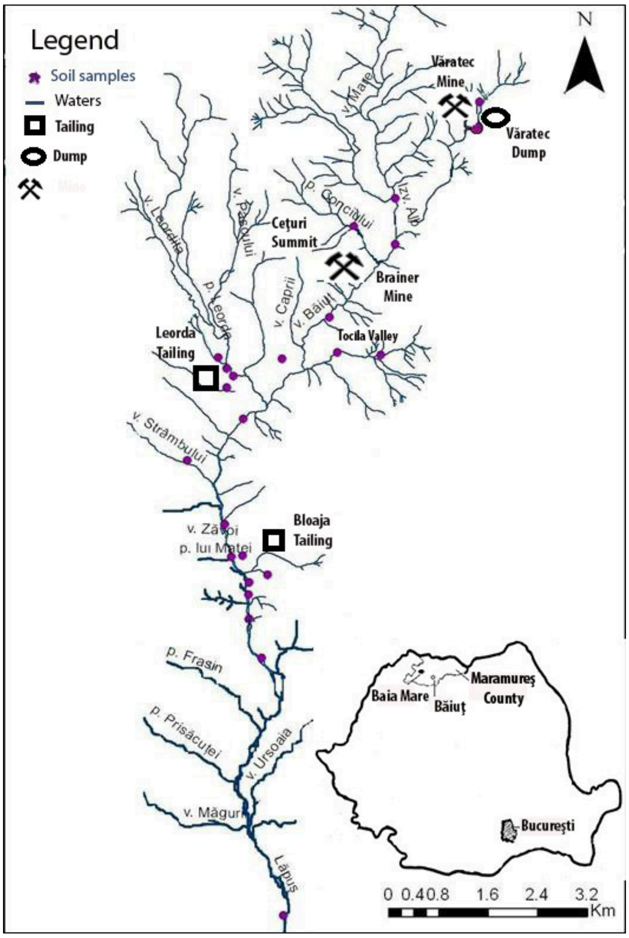


Figure 1. Baiut site, located in Baia Mare Mining Region

Post-tectonics sedimentary rocks are Badenian, Sarmatian and Pannonian age (Edelstein et al., 1971). These rocks are intruded by magmatic bodies, represented mainly by microdiorite pyroxene quartz and pyroxene andesite (Costin, 2000).

Morphological appearance of the perimeter is characterized by rugged mountainous, creeks in the area having a longitudinal profile, with steep, with numerous rapids and falls, leading to high rainwater speed. Streams in the area fed mainly from rainfall and snowmelt and in part from groundwater sources. The flow of these streams is relatively low, draining sometimes in the fall; leakage genesis is directly related to rainfall in the area.

Sources of soil pollution with heavy metals identified in Băiuţ are tailing dams, mine waste dumps, mine waters.

3. MATERIALS AND METHODS

Soil samples were analyzed by atomic absorption spectroscopy with ContrAA® 700 Analytik Jena apparatus for the determination of heavy metal and by X-ray diffraction to determine the mineralogical composition Philips difractometer with PW 1043/01 tub, Ni filter and X Muller Mikro 101 generator. Atomic absorption spectrometry analyzes were performed in the North University Center and Acme Analytical Laboratories in Vancouver Ltd.

The results for the soil samples were processed to obtain statistical parameters and distribution graphs. In order to obtain statistical parameters, graphs, and histograms were used the following softs Office 2007, Office 2010 and NCSS 2007. Heavy metals spatial distribution maps were carried out with ArcGIS software (ArcMap 9.3) using the IDW interpolation method (Inverse Distance Weighting).

4. SOIL CHARACTERIZATION

Soil is an open system capable of handling all functions of ecosystems (Boul et al., 2003). Solid components of soil control heavy metals concentration, trough sorption-desorption processes and dissolution-precipitation (Hlavay et al., 2004). Thus, each soil type is characterized by a specific vulnerability to pollution by heavy metals. Soil organic matter play a very important role in the retention of heavy metals (Barančíková &. Makovníková, 2003).

The study area is covered by different soil types, namely Eutricambosol, Lithosol, Luvosol, Andosol, Regosol, Aluviosol, Dystricambosol. Following the researches in the area is noted that the dominant types are: Lithosols, Aluviosols, Dystricambosol (Fig. 14).

Dystricambosol typical profile Ao-Bv-R is formed by sedimentary rocks of Botiza flysch. They occur in the southern part of the perimeter and on the interfluve between Tocila Valley and Văratec Valley. This soil type also develops in the south west of the Văratec Mountain developed on quaternary deposits, diluvium type. Lithosols, profile Ao -R formed on sedimentary rocks of the Tocila Secu flysch from Botiza Nape, with various exhibitions.

Andic Lithosols develops on such perimeters where the parent material is represented by volcanic rocks, subvolcanic rocks and pyroclastic rocks. They appear in Văratec massive on the interfluvial Tocila – Văratec, on Conciului Valley (Baths) and the top hill Ceturi. Aluviosols develops on Lăpuşului Valley downstream of the confluence with Tocila Valley. They formed on alluvial deposits represented mostly by gravel and sand where are predominant the sedimentary rocks fragments.

5. HEAVY METALS IN SOILS

Heavy metals are retained in soils by complex mechanisms, under the influence of organic and inorganic components of the soil and its physical and chemical properties (Ashraf et al., 2012). Heavy metal complexing reactions with organic and inorganic ligands affect their bioavailability and toxicity (Violante et al., 2010). In soil environments, sorption/desorption reactions as well as chemical complexation with inorganic and organic ligands and redox reactions, both biotic and abiotic, are of great importance in controlling their bioavailability, leaching and toxicity.

The solubility of the metals in the solution depends on the pH of the soil, the oxidation state of the metal components and the redox state of the system where heavy metals are. In general, heavy metals have high affinity for organic compounds from the organic horizons (upper soil horizons), for iron and manganese oxyhydroxides, for the fine fraction, the clay from the soil composition (Alloway, 1995). Heavy metals retention in the soil depends on factors as the nature of the mineral and organic constituents, on the metal provenience, the composition of the soil solution and the pH and Eh (Şipoş, 2009).

The content of heavy metals in the soil depends on the type of the original parent material, where those soils were formed, later, by primary mineral alteration, in different weather conditions, different pedogenic processes have been shown, which determined the migration, or accumulation of heavy metals in soil. The total forms concentration of heavy metals, in different types of soil, reflects different pollution rates, on the soil profile, depending on the type of the metal (Damian et al., 2008).

From the research area, where collected 28 soil samples which were analyzed for the heavy metal content. The results of such analysis being found in table 1.

Table 1. The heavy metals content in soils from the Băiuț mining area

Samples	As	Cu	Cd	Zn	Pb	Ni
	(mg/kg)					
PI1	50.600	208.400	0.930	821.000	573.000	38.780
PI2	23.100	176.980	1.188	341.600	489.800	22.000
PI3	266.700	829.500	13.040	1264.500	2752.000	43.050
PI6	0.009	27.720	0.870	285.600	49.360	21.740
PI7	217.400	315.200	3.410	474.800	1392.800	7.600
PI8	0.008	40.180	0.896	398.600	197.840	18.160
PI9	0.004	172.000	3.240	569.600	570.000	37.780
PI10	0.007	131.860	3.252	593.200	804.600	26.600
PI11	150.020	174.920	0.374	458.000	807.200	26.980
PI13	0.008	125.240	2.654	536.000	241.800	92.780
PI14	0.007	26.940	0.658	364.000	110.200	1.520
PI16	0.006	61.760	1.036	360.000	191.400	104.280
PI17	0.007	66.480	2.956	298.400	108.420	116.360
PI18	15.430	29.180	0.124	199.160	49.240	126.960
PI19	53.260	21.420	0.472	537.000	6362.000	21.520
PI20	3.330	92.240	2.480	389.600	420.400	49.120
BF02	78.700	324.000	2.570	777.000	325.000	45.900
BF01	73.000	304.000	2.620	674.000	423.000	52.500
PI23	50.420	95.740	1.840	303.200	2600.000	19.140
PI22	90.060	34.460	0.644	234.400	51.300	104.140
PI21	5.734	39.660	0.876	237.800	88.160	77.680
PI25	27.160	23.860	0.200	196.540	70.020	13.360
PI27	31.900	17.230	0.130	101.120	18.980	7.930
PI28	97.114	2184.120	20.915	2834.735	2372.950	71.975
PI29	189.614	1450.200	5.560	758.407	2225.925	97.627
PI30	36.743	279.520	0.245	157.709	311.625	311.410
PI31	66.930	771.550	1.531	170.930	45.370	76.545
PI32	16.940	81.190	0.405	126.944	90.000	195.000

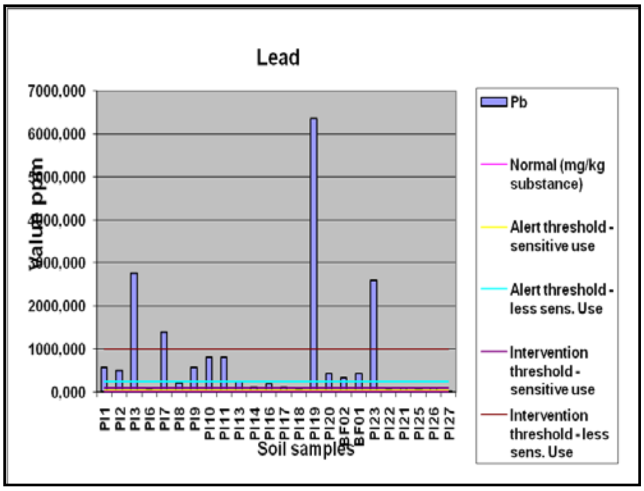


Figure2. Lead distribution in soil

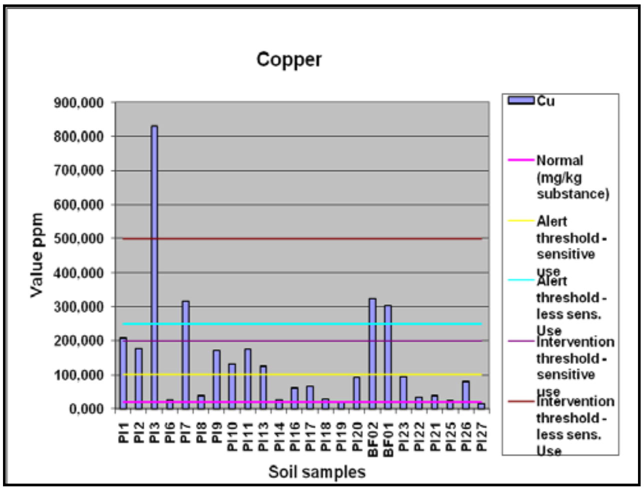


Figure 3. Copper distribution in soil

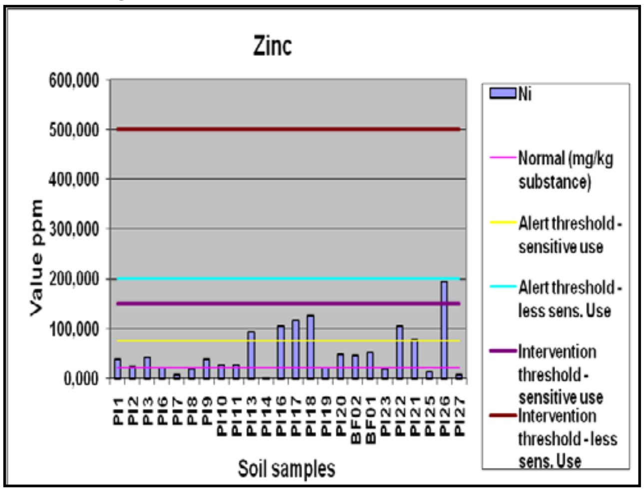


Figure 4. Zinc distribution in soil

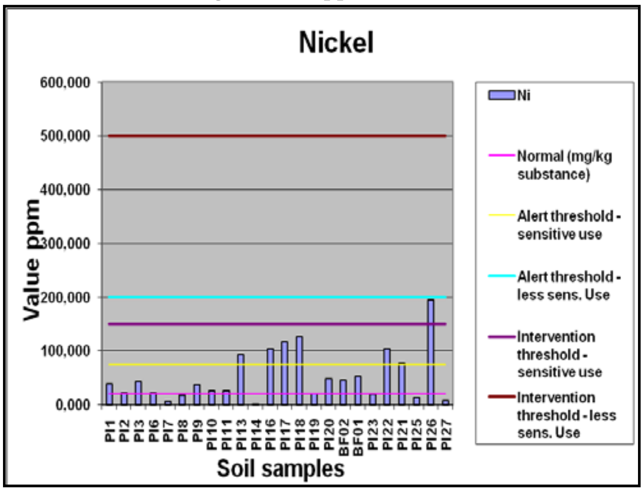


Figure 5 Nickel distribution in soil

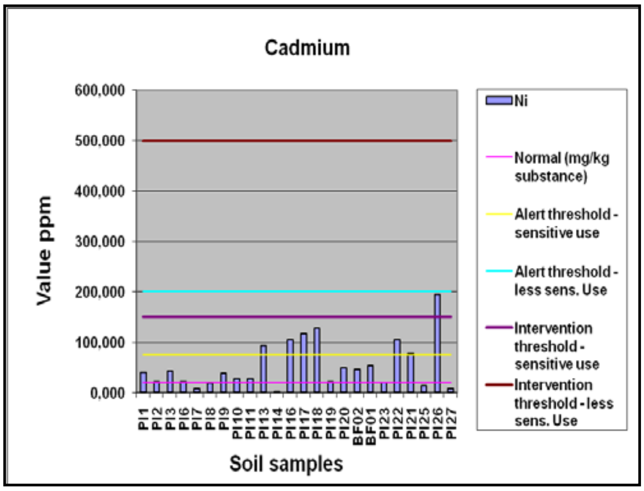


Figure 6. Cadmium distribution in soil

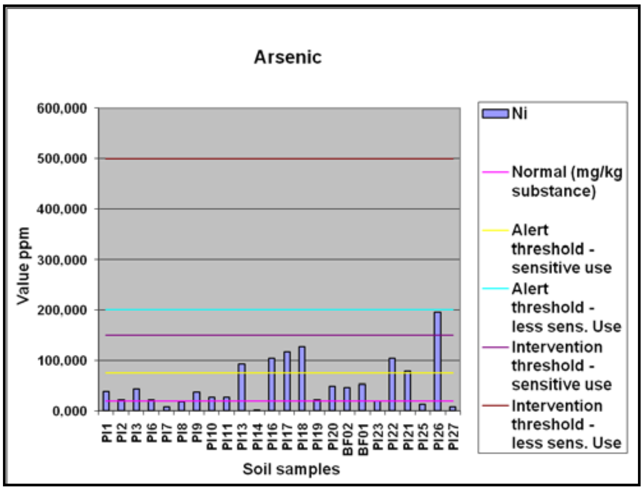


Figure 7. Arsenic distribution in soil

For the interpretation of the heavy metals content levels (mg/kg) in the analyzed soils, we used standardized values of normal thresholds, the maximum allowable limits, alert and intervention thresholds for sensitive soils under Order 756/1997.

After analyzing the chart of lead distribution in soil, is observed a maximum value of 6362 mg/kg and a minimum value of 49 mg/kg (Fig. 2). Lead concentrations exceed normal value in soil, in all the samples. A percentage of 40% of soil samples exceed lead alert threshold, for less sensitive land uses and in four cases can be observed the exceedances of intervention threshold, for less sensitive uses.

The copper concentration area (Fig. 3) falls between a minimum value of 17.23 mg/kg and a maximum value of 829.5 mg/kg. A single sample exceeds the intervention threshold for less sensitive use, near the gap of Bloaja II tailing. Normal values are exceeded in 99%.

From figure 4 representing zinc distribution there is a maximum of 1264 mg/kg and a minimum value of 101.12 mg/kg, for the sampling interval of 0-20 cm. Concentrations of this element in the soil exceeds the normal value, in all the samples and most of the samples exceed warning thresholds. There are no exceedances of intervention threshold for less sensitive uses.

Nickel concentration falls between a minimum of 1.52 mg/kg and a maximum value of 195 mg/kg (Fig. 5). The normal values are exceeded by approximately 60%. There are no exceedances of alert and intervention thresholds for less sensitive use for nickel.

When analyzing the graph of the cadmium concentrations distribution, in the soil, there is a maximum value of 13.04 ppm and a minimum value of 0.124 mg/kg, for 0-20 cm sampling interval (Fig. 6). Concentrations of this element in the soil exceed the normal value in 35%, but most samples being placed under alert and intervention thresholds. No exceedances of intervention thresholds, for less sensitive uses, but a single event near the gap of the Bloaja II tailing.

The concentration of arsenic in the soil falls between a minimum value of 0.004mg/kg and maximum of 266.7 mg/kg. Normal values are exceeded in 51% and alert and intervention thresholds in 24% of the samples. From the results it can be concluded that the amount of arsenic in most cases exceeds the normal values, in 40% of cases exceeds including alert and intervention thresholds (Fig. 7).

By means of the software Statistica 8 the following parameters were calculated: mean, median, minimum, maximum, the lower quartile, upper quartile, coefficient of variation (cv), the standard deviation (**σ**), the skewness and kurtosis (Table 2).

Through Statistica 8 were calculated the correlation coefficients (Table 3). Pearson coefficient indicates association between the analyzed variables, showing the direction and the variation of a variable in relation to the other variable. Pearson coefficient is between -1 and +1 (positive or negative coefficients).

For a large number of samples the most significant correlations were obtained between Zn and Cd (0.9), Cu and As (0.5), Pb and As (0.41). Considering the average concentration for each element, we find the following abundance Pb> Zn> Cu> Ni> As> Cd. Were calculated minimum and maximum values for each analyzed element.

6. GIS MODELING. HEAVY METALS DISTRIBUTION MAPS

Spatial distribution maps of pollutants were conducted with ArcGIS software (ArcMap 9.3) and the interpolation method used was IDW (Inverse Distance Weighting).

Table 2. Soil samples statistical results

Element	Mean	Median	Minimum	Maximum	Lower quartile	Upper quartile	**σ**	cv (%)	Skewness	Kurtosis
As	55.2	29.5	0.00	266.7	0.01	75.9	71.3	129.3	1.7	2.4
Cu	289.5	110.5	17.23	2184.1	37.1	291.8	486.6	168.1	2.9	8.9
Cd	2.7	1.1	0.12	20.9	0.56	2.8	4.4	163.3	3.3	12.0
Zn	516.6	376.8	101.12	2834.7	236.1	581.4	522.8	101.2	3.5	14.8
Pb	847.9	318.3	18.98	6362.0	89.1	805.9	1362.7	160.7	2.8	9.5
Ni	65.3	44.5	1.52	311.4	21.6	95.2	66.1	101.3	2.2	6.4

Table 3. Pearson correlation coefficients of heavy metal in soil*

	As	Cu	Cd	Zn	Pb	Ni
As	1	0.5259	0.4748	0.3864	0.4166	-0.1075
	p= ---	p=.004	p=.011	p=.042	p=.027	p=.586
Cu	0.5259	1	0.8587	0.8273	0.3166	0.0827
	p=.004	p= ---	p=.000	p=.000	p=.101	p=.676
Cd	0.4748	0.8587	1	0.9346	0.356	-0.0517
	p=.011	p=.000	p= ---	p=.000	p=.063	p=.794
Zn	0.3864	0.8273	0.9346	1	0.3898	-0.1256
	p=.042	p=.000	p=.000	p= ---	p=.040	p=.524
Pb	0.4166	0.3166	0.356	0.3898	1	-0.2029
	p=.027	p=.101	p=.063	p=.040	p= ---	p=.301
Ni	-0.1075	0.0827	-0.0517	-0.1256	-0.2029	1
	p=.586	p=.676	p=.794	p=.524	p=.301	p= ---

*significant correlation are for p < .05000, N=28

After analyzing the distribution maps can be seen higher metal concentrations in soils than in the sterile dumps. They are driven by rain and accumulated in the river. In addition to sulfur can be accumulate the goethite, which has the ability to accumulate heavy metals (Horvath et al., 2009). Rainfall help mobilize various metals leached from mine waste dumps.

After analyzing the distribution map for copper in soil, it outlines very clearly the pollution most affected areas (Fig. 15).

High levels in the soil appear near Văratec dump and downstream Bloaja II and Leorda tailings. In the development area of the investigated soils, the maximum copper concentration is observed in the NE part of the study area. The presence of high levels of copper in soil is due to major sources of contamination (Chaoyang et al., 2009). In the northeastern part of the investigated area is Văratec dumps. The Văratec dump was identified frequently chalcopyrite, that explaining the high values for copper. Chalcopyrite alteration is a permanent source of soil pollution downstream of the dump. The maximum was reached near Bloaja II where was the gap, where the deposited material was transported across the road, reaching the river, burning all vegetation in its path and causing strong soils and sediments pollution. The pollution may be due to accumulation over time of mobile compounds of copper in Aluviosol of Băiuţ Valley, as the valley slope is very low here.

Concentrations of copper, whose values are averages from the south, may be caused by expansion of the influence of pollution dumps material transported by surface waters. The area in which the concentrations of Cu are low, below the maximum allowed, corresponding to Lithosol, Regosol and Dystricambosol, developed in areas where the slope and copper mobilization was due to runoff. Retention may be due to copper in the ground formation of insoluble complexes (Gale et al., 2004).

By analyzing lead distribution map and the concentrations chart clearly appear two polluted areas, namely downstream of Văratec dump and on the confluence with of Baiut Valley with Conciului Valley, valley that includes some of the most important adits (Fig. 17). Lead behavior in soil is similar because it has low mobility and high density and it is understandable it's presence near the sources of pollution. Lead is widely reported to be the least mobile of the heavy metals (Gale et al., 2004).

By analyzing the distribution map of zinc in the soil, higher values appear near Văratec dump and downstream of the two tailing dams, several kilometers distance, the highest value being near the gap from Bloaja II tailing (Fig. 16). Downstream of the confluence of Băiuţ Valley with Leorda Brook and particularly at the junction with Bloaja Valley there is a large zinc anomaly, in soils . The increased mobility of zinc in soil at low pH provides metal distribution, with high concentrations at big distances from the pollution sources. Zinc, which is a mobile element, was leachate from the top of the studied area and deposited in Aluviosols, in the area where the valley slope is strongly reduced.

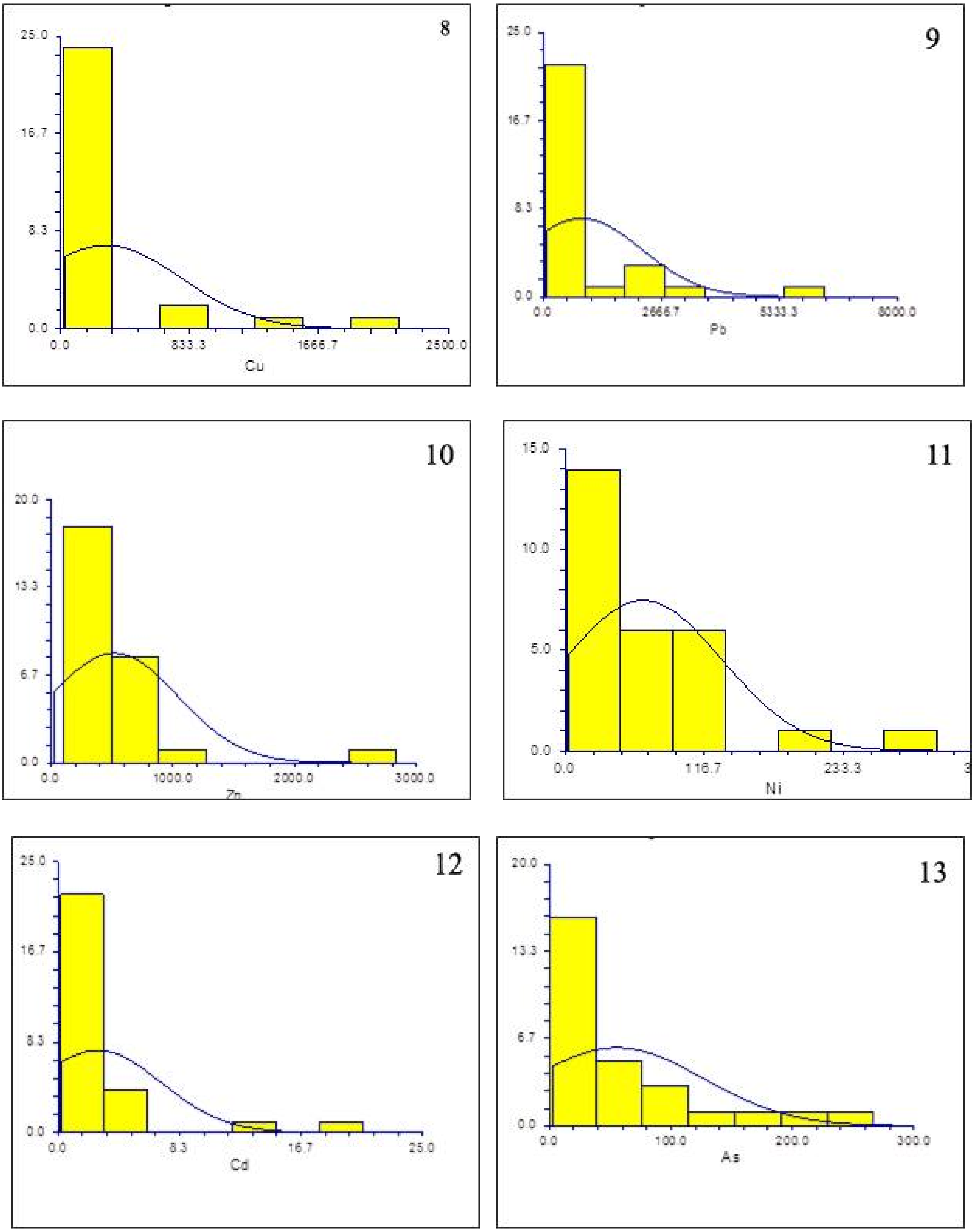
Also zinc mobilization from Bloaja and Leorda flotation tailings dumps, trough water and wind erosion has significantly increased the zinc content in Aluviosols. Both tailings dams are not covered by vegetation and erosion effects are visible.

Low mobility, highlighting maximum concentrations areas in the soil, might be suggested by adsorption and coprecipitation mechanisms in relation to their specific components (Fernández-Caliani et al., 2009). At the confluence of Băiuţ Valley with Conciului Valley there are Petru and Pavel veins, which mainly have a lead and zinc mineralization. High lead contents in the Văratec dump can be explained by the presence of clay minerals, which are designed to retain heavy metals (Sasaki et al., 2002). Distribution histogram, (Fig. 10) has a left asymmetry which explain the high values and standard deviation.

Analyzing nickel distribution map can be seen high concentrations in the Văratec dump, near flotation plant and Tocila Valley. In soil nickel is strongly associated with Fe and Mn oxides (Kabata, 2001) .The highest values for nickel are near Văratec dump.

By analyzing the distribution map of cadmium in soils of Băiuţ mining basin, it outlines very clearly two polluted areas, Văratec dump and tailings dams' area, especially from Bloaja tailing. In Văratec dump have been identified large amounts of sphalerite, which could explain the high cadmium content. The anomaly for cadmium, from tailings area, overlaps the zinc anomaly. Cadmium accumulation in these areas is explained by a higher mobility and convenience of the nearby tailings, which could be mobilized in the soil (Fig. 18). The histogram has an aspect with a strong left asymmetry and a much smaller standard deviation than the other heavy metals in the soil (Fig. 12).

By analyzing arsenic distribution map, emerge clearly the polluted areas, areas that coincide with mining waste deposits as Văratec dump, Leorda tailing dam and Bloaja II tailing dam, an old sterile dump near the former mine buildings. In addition to the four areas, there is still an area with high arsenic concentrations, Băiuţ Valley area, presenting large amounts of arsenopyrite, from Petru and Pavel vein (Fig. 19).



Figures 8, 9, 10, 11, 12,13. Analyzed heavy metals histograms (using NCSS 2007 soft)

Arsenic source is represented by sulphides: tennantite, arsenopyrite and pyrite which may contain arsenic as a substitute for sulfur, which were identified in the Văratec mine dump. A large area of soil pollution with arsenic is in the Bloaja II and Leorda tailing dams. The source of contamination is represented by the sterile deposited in the tailings, which are under continuous precipitation water and wind erosion, but especially pyrite concentrate which is stored in these tailings.

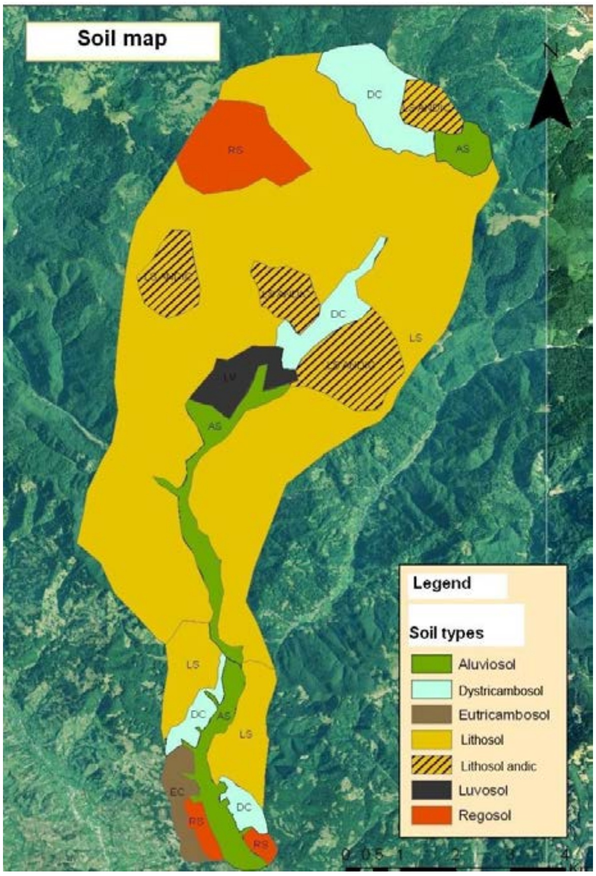


Figure 14. Soil map from Băiuţ area.

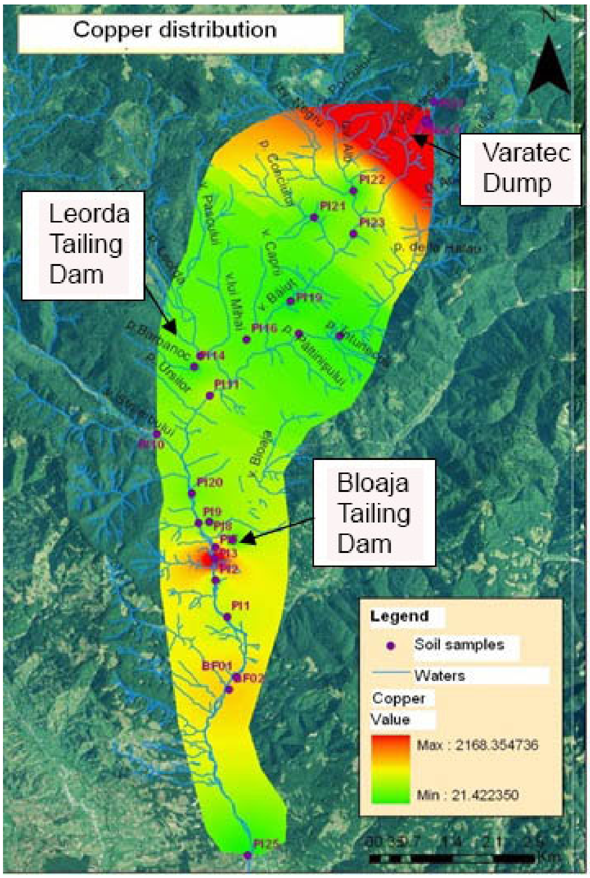


Figure 15. Copper distribution map

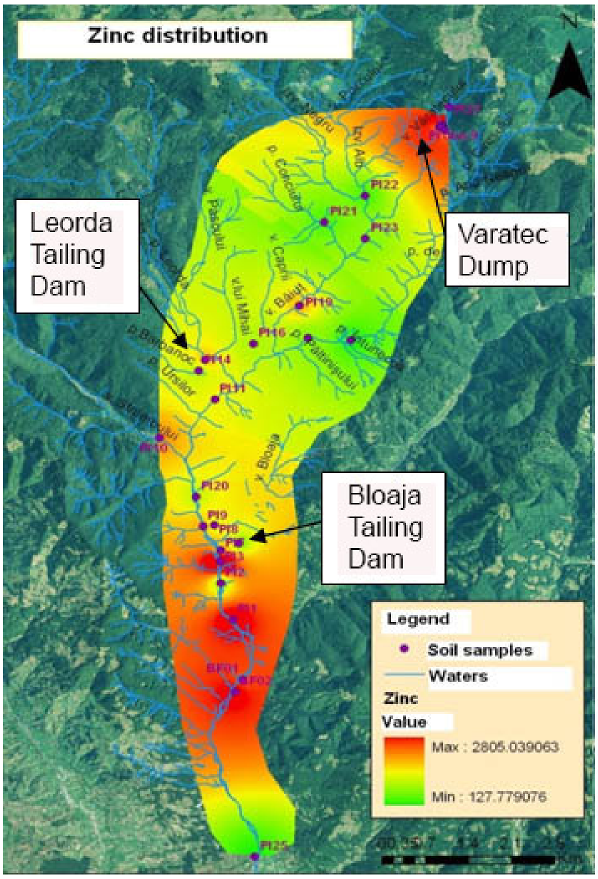


Figure 16. Zinc distribution map

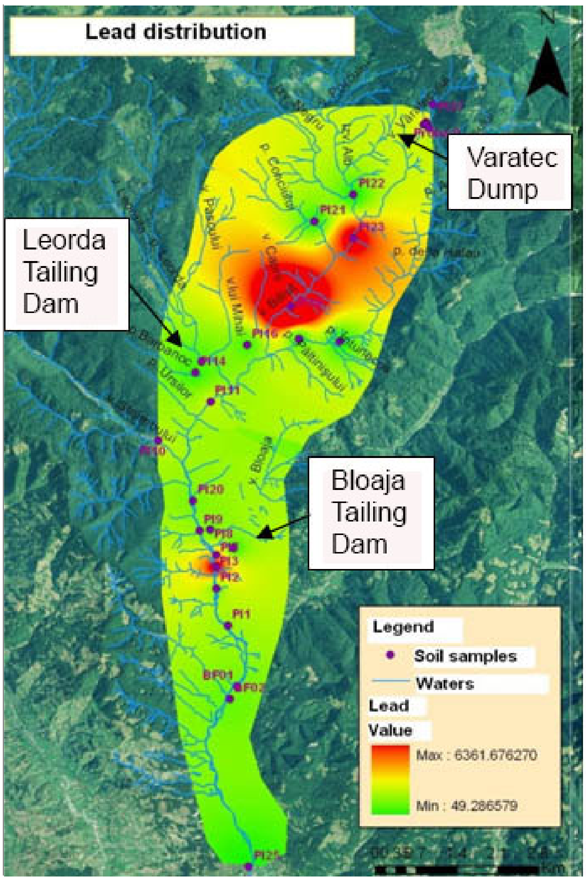


Figure 17. Lead distribution map

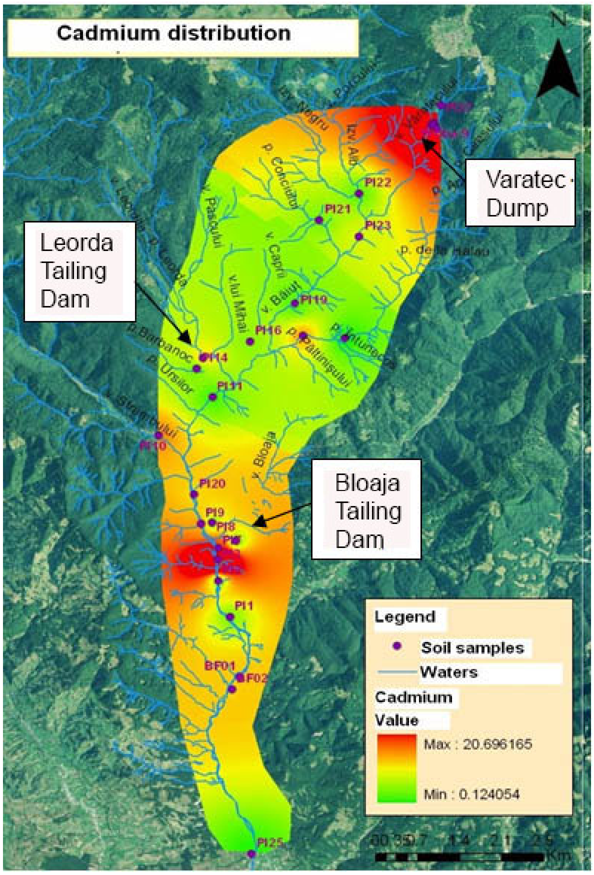


Figure 18. Cadmium distribution map

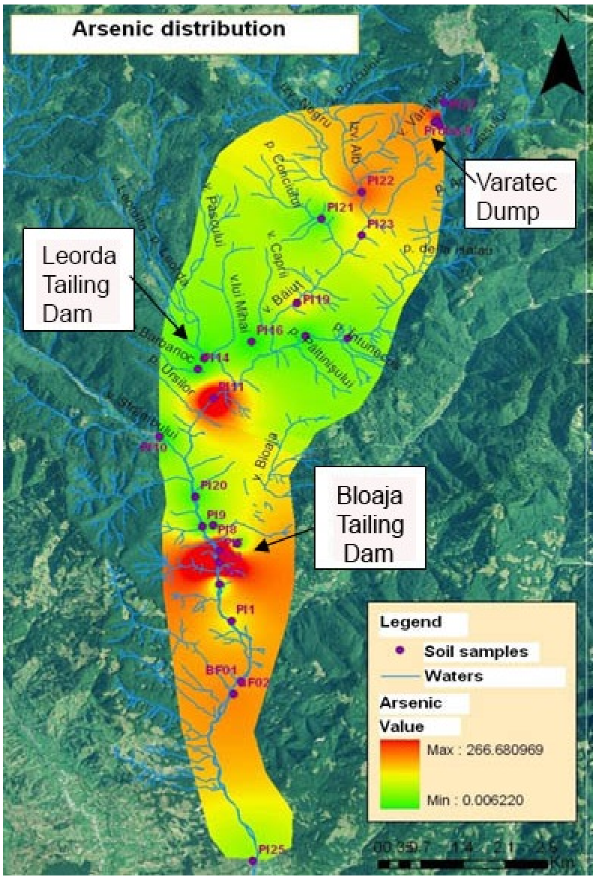


Figure 19. Arsenic distribution map

The presence of heavy metals (Pb, Cu, Zn, Cd), with elevated contents which exceed background concentrations and specific ones in Băiuţ area due to pollution by geo - mining activity. The source of the metals, a base metal ores were mined in the region for a period of about 600 years.

Heavy metals in soils are taken from surface water are introduced into the water network and thus reach the trans boundary river basin, fact that contributes to cross-border areas pollution. Heavy metals reach the soil and their behavior depends on the chemical and physical properties of the soil, as well as their origin.

Analyzing the distribution maps for all of these elements (Cu, Pb, Zn, Cd, As) in soil show high values, highlighting exceedances of alert and intervention thresholds in some areas, namely near Văratec dump, downstream of the two tailings dams, a few kilometers away and in the gap right in front of Bloaja II tailing. These high concentrations are closely correlated with pollution sources.

High concentrations of heavy metals in soil can be attributed to their accumulation in organic horizon of the soil. After analyzing the distribution map for copper in soil indicator, it outlines very clearly the areas most affected by pollution. High levels occur in the soil of Văratec dump area and downstream Bloaja II and Leorda tailings.

The area, in which the concentrations of Cu are low, below the maximum allowed, corresponds to the soil type Lithosol, Regosol and Dystricambosol and overlaps with areas where soils are used for orchards, livestock, grazing and forestry.

7. CONCLUSIONS

In accordance with the specified limits, the content of heavy metals (Pb, Cu, Zn, Ni, Cd, As) in total forms proving their high accumulation in soils. After the analysis on samples from the surface of Văratec dump can be observed very high values for Cu, Pb and Zn.

The presence of high concentrations of Cu in the soil, in the northeastern part of the investigated area, suggesting the major sources of contamination (Damian et al., 2007) represented by the mine Văratec dump. In the Văratec dump was identified frequently the chalcopyrite explaining the high copper values.

Analyzing distribution maps for all elements clearly appear heavily polluted areas, which are located near sources of pollution, waste dumps and tailings dams. The main environmental impact of Băiuţ Văratec mine consists of soil contamination with heavy metals through acid mine drainage. High permeability of the host rocks makes meteoric water to easily reach the underground. The high content of sulfur, especially of iron and the small size of the mineral grains favor the oxidation reactions and, consequently, higher concentrations of heavy metals. Considering all presented factors and elements clear that the studied mining area - Băiuţ is heavily polluted. The land in the area, some with high overflow thresholds for heavy metals have different uses, including temporary grazing, permanent pasture (winter stables), orchards and vegetable gardens.

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