Geo -Spatial Quantification of Negative Effects of Mining Activities on Sediments and Especially on Soils from Băiuț Mining Basin, Maramureş

Summary of doctoral thesis NĂPRĂDEAN Ioana Maria married as CHIRA

Content

Introduction	6
Chapter I. Localization and characterization of the study area in September	6
I.1. The geographical position	9
I.2. Soils	10
I.3. Water resources	10
I.4. Climate of the region	10
I.5. Rainfall	12
I.6. The winds	12
I.7. Biodiversity and Protected Areas. Natura 2000	12
Chapter II. Methodology	15
II.1.Sampling	15
II.2.Preparation of the samples and analyses	17
II.3.Processing analytical data and mapping	18
Chapter III. Framing Băiuț zone in Oas - Gutai metallogenetic area -Ţibleş	19
Chapter IV. Geology	24
IV.1. Sedimentary formations .	24
IV.2 . Micro - tonalitice \leftrightarrow micro granodioritic rocks	28
IV.3. Rocks micro diorite \leftrightarrow porphyritic quartz (with pyroxene and biotite)	29
Chapter V. Metallogenesis	30
Chapter VI. Description of metallogenetic mineralization from Băiuț – Văratec Field	33
VI.1. Metallogenetic Structure of Băiuț - Brainer	34
VI.2. Metallogenetic Structure of Văratec	36
Chapter VII. Mineralogy	39
Chapter VIII. Identifying potential environmental issues, raised by the	
Băiuț Mining area	45
VIII.1. Mining Pollution. Theoretical premises	45

VIII.2. Pollution sources inventory	51
VIII.3. Sterile dumps	52
VIII.4 . Tailing dams location	54
VIII.5. Mine closure or mining abandon?	55
Chapter IX. Influence of the mineralogical composition of the mineralization	
related to soil pollution with heavy metal, in the Băiut region	60
Chapter X. Văratec dump	70
X.1. Granulometry of sterile samples	71
X.2. Microscopic description of rock's fragments	72
X.3. Mineralogical analyses on ore samples	78
X.4. Varatec dump geochemistry	83
Chapter XI. Leorda and Bloaja tailing dams	92
XI.1. The results of mineralogical investigations	92
XI.2. The metal content in tailing dams	95
XI.3. Mineralogy of pyrite concentrates	96
XI.4. The metal content of concentrates	98
Chapter XII. The sediments of Băiuț Valley	100
XII.1. Mineralogical composition	101
XII.2. The chemical composition of the sediments	101
Chapter XIII. Soils in the Băiuț mining basin	106
XIII.1. Soil description	106
XIII.2. Soil geochemestry	108
Chapter XIV. Polutants distribution maps in sediments and soils using GIS modeling	119
Chapter XV.Conclusions	130
Bibliography	138

Motto: "We shan't save all we should like to –but we shall save a great deal more than if we never tried." Sir Peter Scott

INTRODUCTION

Mines and associated waste sites are point sources of pollution and their impact generally occurs locally. In terms of the spatial activity of ores, is only the natural resource sector, in addition to groundwater extraction, whose activities and environmental impact falls in underground three-dimensional space (Jordan and D' Alessandro, 2004).

Soil pollution is one of the key issues requiring priority resolution.

Recent studies regarding soil pollution were performed by Damian et al., (2007), Damian et al., (2008), Damian et al., (2010), Andras et al., (2008), Horvath et al., (2009) Stumbea, (2010), Prundeanu & Buzgar (2011), Balaban et al., (2011).

Based on the above considerations, this paper aims to assess the negative effects of the mining operation, in a small mining area Băiuţ - Văratec, based on detailed geochemical and mineralogical analyses carried out on sediment samples, soil samples of ore and mine tailing dams.

Mining, together with its specific activities, has a significant impact on the environment, with local dominance, near the mine area and near the mines deposits and mining waste products from the extraction and processing activities.

In order to achieve the goals and objectives presented at the beginning of the paper, a detailed description of the studied area was done, since each factor has its role in the complex process of mining and mining pollution. We have analyzed the location, the shape of the basin, the climate, biodiversity and protected areas, geology and metalogenesis, mineralization description and ore mineralogy.

In order to determine the level of pollution and its causes was needed a detailed description of the existing natural background area.

Total concentration of metals in sediments and soils is determined by geological background, geochemical processes and anthropogenic sources. The intensity of these factors varies, depending on the region, which causes a spatial variation of the total metal concentration.

The studied area is Băiuț mining zone, superimposed on Băiuț Valley basin, which is a small basin, whose waters flow into the Lapus River.

Personal contributions are : inventory of pollution sources for the study area , reporting the visible effects of early mining in some galleries and ponds, soil map , mineralogical and geochemical description of Văratec dump and Leorda and Bloaja II tailing dams, determination of concentrations for heavy metals and arsenic in sediments of the Băiuţ Valley , determine the concentrations of heavy metals and arsenic in soils , achieving spatial distribution of heavy metals , especially Cu, Pb , Zn , Cd , Ni and As and testing to compare the behavior of pollutants in sediments and in soils .

The research was conducted in Băiuț Zone, from the Baia Mare district. Baia Mare mining district is part of the Carpathians, which is a continental arc of Neogene age.

Sources of sediments and soils pollution with heavy metals identified in the Băiuț are the flotation tailing dams, mine waste dumps, mine waters.

Ore exploitation from Băiuţ was done through nearly 30 galleries, among which the most important are Brainer, Văratec, Petru and Pavel, Hell, Cisma. Mining waste deposits (numerous dumps, the largest of all is Văratec dump), mining galleries (30 galleries, among are Brainer, Văratec, Petru and Pavel, Hell, Cisma), mine waters and flotation deposits (four tailing dams) are sources of pollution for the studied area, Băiuţ Valley , with its tributaries .

Abandoned mines in historical sites are a particular problem because of the long-term environmental damage. Abandoned mines are the same as active mines in the types of hazards and potential environmental impact. Băiuț mining area has abandoned mines and the largest and the most important of these is Văratec mine.

Băiuţ - Brainer ore deposit is bounded in the two main vein fractures: Divine Providence - called Băiuţ - and Robu - located northwest of the first. Characteristic for this structure and for those at East of it, is partial lack of the andesitic board, the veins coming out in the vicinity of andesite intrusions, microdiorite and micromonzodiorite.

The two major groups of minerals founded in the Băiuţ - Brainer - Văratec mining area are metallic minerals and gangue minerals. In the mineralogical composition of the ore participate: native elements, sulfides, sulphosalts, tungstates, oxides and hydroxides, carbonates, sulfates and silicates. The main metallic minerals encountered are : pyrite , marcasite , arsenopyrite , sphalerite , galena , chalcopyrite , bismuthine , tetrahedrite , bournonit , semseyit , sulphosalts,, bismuth . Gangue minerals are represented by quartz, carbonate, barite, fluorite, clay minerals, and adularia. Of gangue minerals were identified quartz, carbonates (calcite , dolomite , siderite) , silicates (kaolinite , adularia) and sulphates (barites) .

During the investigations and sampling conducted on the Văratec mine dump were identified many fragments of ore deposited at various stages. Most of the fragments were identified on the route of the railway transport mining removed when sampling in the south west near the roll ore transhipment takes place and where the funicular line is. Were identified parallel textured ore fragments, which consists of alternating bands of metallic minerals rich in sphalerite and galena, quartz, carbonates and clay minerals nests associated with carbonates. Another type of ore fragments contains large quantities of red quartz with oligist hematite. In the south - western part of the dump there is a large amount of ore, largely deposited when the mining activity was stoped. These fragments are composed of ore rich in chalcopyrite, and also sphalerite and galena -rich fragments. Identified fragments are, in

majority, from Văratec veins demonstrating the existence of pollution throughout the mining activity.

From chemical analyzes point of view, performed on the Văratec dump material, normal values are exceeded in the majority of analyzed indicators, in most cases alert and intervention thresholds being exceeded.

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

Other sources of pollution from the studied area are Bloaja II and Leorda tailing dams. On these tailing dams have carried out mineralogical investigations and chemical analysis. The mineralogical composition of the tailing dams is similar to the main components of nonmetallic mineral veins. Quartz is the predominant mineral compound. Quartz' source is the gangue of the veins from Băiuţ, Quartz can originate from Tocila - Secu flysch formations, where frequently occur in sandstone formations. Carbonates are represented by calcite and dolomite. Feldspars derived in particular from igneous rocks. Many of the Băiuţ veins are confined to microdioritice and microtonalitice bodies containing phenocrysts and feldspar microcrystals. Feldspars and sandstone were also having as source Tocila Secu formation and Sarmatian formations. Clay minerals are represented, in particular, by kaolin, as revealed by X -ray diffraction analysis. Kaolinite frequently occurs as a gangue mineral in the upper part of the veins and, in particular, in Botiza and Văratec group veins.

Pyrite occurs frequently in decantation tailing dams, and in contact with water, by alteration and chemical degradation, can influence its pH, generating AMD. Pyrite is present in abundance in the form of microscopic grains, overgrown with quartz or as micro inclusions in igneous fragments. In addition to pyrite may appear small amounts of marcasite. Many pyrite grains pass through supergene alteration in iron oxyhydroxides.

As shown in both tailing dams there are appreciable quantities of copper, lead, zinc and arsenic, which is due to the similar mineralogical composition to the deposited material from the same reservoir.

Consequence of the presence of minerals containing metal sulfides (pyrite, chalcopyrite, arsenopyrite), by exposing them to the aerobic environment, is generation of ARD, that allow release of metal ions in solution and then their migration.

On Bloaja II and Leorda tailing dams there are deposited pyrite concentrates. They are eroded by rain water and represents a constantly source of heavy metal pollution. By weathering and chemical degradation can influence its pH, generating ARD. From Bloaja tailing dam were washed large amounts of pyrite, which have come down in the Lăpuş River, strongly affecting vegetation. They generated large amounts of acid waters that have accumulated on the tailing dam.

In close connection with the parental material of the veins, can be observed high concentrations of heavy metals and arsenic, and in particular, high content of lead and zinc, especially, in the case of the Bloaja II concentrate. Large amounts of lead and zinc are due to the presence of galena and sphalerite.

Heavy metals (Pb, Cu, Zn, and Cd) with elevated contents exceeding background concentrations and those of the specific area, due to geo - mining activity pollution. The source of these metals is represented by polymetallic ores, exploited in the region for a period of about 600 years. Heavy metals from soils are taken from surface water are introduced into the water network and thus reach the transboundary river basin, being part of cross-border pollution areas.

Accumulations of sulphides contain sulphides, especially pyrite and marcasite. Under aerobic conditions and in the presence of bacteria, through the oxidation of sulphide it is formed the sulfuric acid. In this way appears acid drainage, which is a major source of environmental pollution.

The contents of heavy metals from Văratec dump don't have a uniform distribution. There are samples with high content of heavy metals, especially those taken from the dump platform and the railway alignment. The large contents are for copper, lead and zinc. There are appreciable content of arsenic, antimony and cadmium.

The accumulation of heavy metals in sediments is dominated by the combination of metal oxides, especially under aerobic conditions. The mineralogical composition of the sediments reflects better the rocks from the source area, including the composition of the Băiuț mineralization. Predominant mineral components are represented by quartz (30-50 %), feldspar (3-15 %), together with clay minerals (montmorillonite, kaolinite, illite) and goethite.

In sediments, heavy metals are able to endanger the ecosystem when they are remobilised. A big part of the heavy metals reached the waters and accumulated in sediments and possibly in living organisms.

Distribution of heavy metals in sediments shows that pollution is due to several sources, both upstream areas (Văratec area) and downstream from Leorda and Bloaja II. High concentrations of metals in sediments, especially Cu, Pb and Zn, clearly demonstrates the human impact on Băiuț basin, exceeding by far the natural background values and those

considered normal for sediments . Heavy metals, from the mentioned sources, end up in the soils , and their behavior depends on the chemical and physical properties of the soil , as well on their origin.

Using statistical soft STATISTICA 8 the following parameters were calculated: mean, median, minimum, maximum, lower quartiles, upper quartiles, standard deviation, and asymmetry. Considering the average concentration for each element, we find the following abundance Pb > Zn > Cu> Ni > As> Cd. 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).

In both analyzed tailing dams (Bloaja II and Leorda) appear appreciable quantities of copper, lead, zinc and arsenic, which is due to similar mineralogical composition, the deposited material was from the same deposit.

Analyzing the distribution maps for these elements (Cu, Pb , Zn , Cd , As) in sediments and soils, appear high values showing exceedances of alert and intervention thresholds in some areas of the study zone , namely the Văratec dump, downstream of the two tailing dams, a few kilometers away and right in front of the Bloaja II tailing dam gap. All of these high concentrations are closely correlated with pollution sources.

After analyzing the distribution maps made for sediments and soils samples can be observed higher metal concentrations in sediments and soils than in the waste rock dumps. These high contents are in large quantities because in sediments accumulates heavy minerals (all sulphide mineralization occurring at Băiuţ - Breiner and Văratec). They are driven by rain and accumulated in the river. High metal concentrations in the river sediments suggests that accumulated heavy metals were absorbed by secondary minerals, formed in the area, such as goethite. Regarding the distribution of heavy metals and arsenic in sediments, we can say that they have an affiliation for sulfides and goethite and they tend to accumulate. High concentrations of heavy metals in soils can be attributed to their accumulation in organic soil horizon.

After analyzing the distribution map for copper in soils, it outlines very clearly the areas most affected by pollution. Comparing the two maps of distribution for Cu- sediments from the Băiuţ valley and adjacent soils can clearly see the influence of surface pollution sources. High levels in the soil appear to Văratec dump and downstream of Bloaja II and Leorda tailing dams.

The area, in which the concentrations of Cu are low, below the maximum allowed, corresponds to the development of soil types: litosol, regosol and districambosoil and overlaps with areas where soils are used for orchards, livestock, grazing and forests.

The distribution map of copper in sediments reveals us three areas with very high values, which are: downstream of Văratec dump, at the confluence of Conciului Valley and Băiuţ Valley and downstream of the Leorda tailing dam.

By analyzing the distribution map for lead and the chart of lead concentrations arise, clearly, two polluted areas, namely downstream Văratec dump and the confluence of Băiuţ Valley with Conciului Valley, valley that includes some of the most important galleries. Lead concentrates similar in soils and sediments as it has low mobility and high density and is understandable its accumulation near the pollution sources. Lead is widely reported to be the least mobile of the heavy metals

Zinc distribution map in soil differs from the one in sediments. By analyzing the distribution map of zinc in the soil, higher values appears in the Văratec dump area and downstream of the two tailing dams, on a several kilometers distance, the highest value appearing next to Bloaja II tainling gap. Downstream of the confluence of Băiuţ Valley with Leorda Brook and particularly at the junction with Bloaja there is a large zinc anomaly in soils. The increased mobility of zinc in soil and sediments, at low pH, provides metal distribution, with high concentrations at greater distances from pollution sources. Zinc, which is a movable element was leachate from the top of the studied area and applied in alluvisoils in the area where the valley slope is greatly reduced. The mobilization of zinc from flotation tailing dams Bloaja and Leorda, trought water and wind erosion, has significantly increased the zinc content in that type of soil.

There are two anomalies for arsenic in the sediments. One smaller is located downstream from Văratec dump and its source is represented by pyrite and arsenopyrite mobilized from the dump. A second anomaly, much larger is at the confluence of Conciului Valley and Băiuţ Valley.

By analyzing the distribution map of arsenic in soils, emerge clearly the polluted areas, areas that coincide with mining waste deposits, like Văratec dump, Bloaja II and Leorda tailing dams and an old deposit near the former headquarters of the mine. In addition to the four areas, there is still an area with high arsenic values on Băiuţ Valley, area that present large amounts of arsenopyrite from Petru and Pavel vain.

Cadmium accumulation is explained by a higher mobility and the vicinity with tailing dams where it can be mobilized in the soil. Examining the distribution of Cd in sediment, one can see, there is a spread on a small surface downstream of Văratec dump. High concentrations of Cd in sediment may result from material accumulation from mine dumps and organic material. The analysis of distribution maps for all elements, both in soil and sediment, clearly show polluted areas, areas that are close to pollution source like waste dumps and tailing dams.

The main environmental impact of the mine Văratec Băiuţ consists in sediments and soils contamination with heavy metals, through acid mine drainage . High permeability of the host rocks due to intense tecthonization of the geological formations 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.

Analyzing all presented factors and elements show that Băiuţ area is heavily polluted. The lands in the area, some with high exceedance thresholds for heavy metals, have different uses, including temporary grazing, permanent pasture (winter stables), orchards, vegetable gardens.

Applicability of legislation on the protection of soil and subsoil, in particular, and mining closures legislation, is still a matter of financial resources, responsibilities and morality.

Selective Bibliography

- Andras P., Lichy A., Krizani I., Ruskova J., Ladomersky J., Jelen S., Hroncova E.& Matuskova L., (2008), Podlipa Dump-Field at Lubietova – Land Contaminated by Heavy Metals (Slovakia), Carpathian Journal of Earth and Environmental Sciences, 2008, Vol. 3, No. 2, p. 5 – 18;
- Bălăban S.I., Iancu O.G. & Bulgariu D., (2011), The Geochemical Distribution of Heavy Metals for Some Mine Tailings from the Fundu Moldovei Area, Romania, Carpathian Journal of Earth and Environmental Sciences, September 2011, Vol. 6, No. 2, p. 279 – 288;
- Chaoyang W., Cheng W. & Linsheng Y., (2009), Characterizing spatial distribution and sources of heavy metals in the soils from mining-smelting activities in Shuikoushan, Hunan Province, China, Journal of Environmental Sciences 21, p. 1230–1236;
- Chira I., Damian G. & Chira R, (2014), Spatial distribution of heavy metals in the soils of Băiuţ Area, Maramureş County, Romania, Carpth. J. of Earth and Environmental Sciences, Vol. 9, No. 1.
- Costin D. & Vlad Ş., (2005), Ore formation at Văratec-Băiuţ, Baia Mare region, East Carpathians, Romania, Geochemistry, Mineralogy and Petrology, 43, Proceedings of the 2005 Field Workshop, Kiten, Boulgaria, p. 64-68;

- Damian F., Damian Gh., Costin D., (2000), Bismuth sulphosalts in the Neogene hydrothermal vein ores from the Baia Mare Ore District, Acta Mineralogica-Petrografica, Szeged, XLI, Supplementum, p. 27;
- Damian F., Damian Ghe, Lăcătuşu R., Macovei Ghe., Iepure Ghe., Năprădean I., Chira R., Kolar L., Rata L., Zaharia D., (2008), Soils from the Baia Mare Zone and Heavy Metals Pollution - Carpathian Journal of Earth and Environmental Sciences, ISI magazine, -Floarea Vol. 3, No. 1, p. 85 – 98;
- Damian F., Damian G., Iepure G., Napradean I., Kollar L., Chira R. & Zaharia D., (2007), The distribution of the heavy metals in aluviosols from Copsa Mica zone Bulletin Stiintific al Univ. de Nord Baia Mare Vol XX, p. 187-194;
- Damian F., Damian G., Macovei G., Iepure G., Nasui D., Napradean I., Chira R. & Kollar L., (2008), Spatial distribution and mobility of the heavy metals in soils from Baia Mare Area Studia Universitatis Babes Bolyai, AMBIENTUM LIII, vol 53, 1-2/2008,, ISSN:1843-3855, p. 65-72;
- Dorotan D., Chira I. & Jordan G., (2011), Metale grele în aluviuni. Studiu de caz în pârâul Văratec, Băiuț, Ecoterra, no. 26;
- Fernández-Caliani J. C., Barba-Brioso C., <u>González</u> I. & <u>Galán</u> E., (2009), Heavy Metal Pollution in Soils Around the Abandoned Mine Sites of the Iberian Pyrite Belt (Southwest Spain), <u>Water Air and Soil Pollution</u> (impact factor: 1.63). 01/2009; 200(1):211-226. DOI:10.1007/s11270-008-9905-7;
- Horvath E., Jordan G., Fugedi U., Bartha A., Kuti L., Heltai G., Kalmar J., Waldmann I., Napradean I. & Damian G., (2009), Risk assessment of heavy metals in abandoned mine lands as a signifcant contamination problem in Romania., EGU General Assembly 2009, Geophysical Research Abstracts, Vol. 11;
- Jordan G. & D'Alessandro M. (eds), (2004), Mining, Mining Waste and Related Environmental Issues: Problems and Solutions in the Central and Eastern European Candidate Countries, Mining and Mining Waste: Pressures, Impacts and Responses in the Enlarged European Union. Joint Research Centre of the European Commission, Ispra, 2004, p. 169-206 si p. 13-43;
- Kabata Pendias A., (2001), Trace Elements in Soils and Plants Third Edition, CRC Press LLC;
- Mariaș Z. F., (2005), Metalogeneza districtului minier Baia Mare, Model bazat pe sistemul hidrotermal Cavnic (Maramureș),evaluări comparative cu alte sisteme epitermale din lume, Editura Cornelius, 450 p.;

- Năprădean Ioana & Chira Razvan, (2006), The hydrological modeling of the Usturoi valley using two modeling programs - WetSpa and HecRas, Carpth. J. of Earth and Environmental Sciences Vol. 1, nr. 2. p. 53-62;
- Plotinskaya O., Damian F., Prokofiev V., Kovalenker V. & Damian Gh., (2009), Tellurides Occurrences in the Baia Mare Region, Romania, Carpathian Journal of Earth and Environmental Sciences, October 2009, Vol. 4, No. 2, Baia Mare, p. 89 – 100;
- Pop N., Pop V., Gotz A., Damian G., Lepedus M., Grama C., Pop E. & Petrar C., (1984), Studiul geologic complex E. M. Băiuţ, Etapa a Ill-a Mineralizaţii din mina Văratic, Simbol C 3003/1984, ICPMN Baia Mare, Colectivul de geologie şi mineralogie aplicată, Baia Mare;
- Prundeanu I. M. & Buzgar N, (2011), The Distribution of the Heavy Metals and As in Soils of the Falticeni Municipality and its Surroundings, Carpathian Journal of Earth and Environmental Sciences, February 2011, Vol. 6, No. 1, p. 51 - 64;
- Seghedi, I., Balintoni, I. & Szakács, A., (1998), Interplay of tectonics and Neogene postcollisional magmatism in the intracarpathian region Lithos, 45, p. 483-499;
- Sipoş P, (2009), Sorption of copper and lead on soils and soil clay fractions with different clay mineralogy, Carpathian Journal of Earth and Environmental Sciences, October 2010, Vol. 5, No. 2, p. 9 – 18;
- Stumbea D., (2004), The Acid Rock Drainage and its implications on the environment, (I) The Acid Drainage, Analele Stiintifice ale Universitatii "AL. I. CUZA" IAȘI, Geologie, Tomul XLIX-L;
- *****Ordonanța de urgență nr. 57 din 20 iunie 2007 privind regimul ariilor naturale protejate, conservarea habitatelor naturale, a florei și faunei sălbatice;

www.apmmm.anpm.ro

www.biodiversity-maramures.ro

www.esri.com