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HEAVY METAL POLLUTION IN THE LĂPUȘ RIVER BASIN, MARAMUREȘ COUNTY

-PhD thesis Summary-

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Contents

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Introduction and Objectives

The activity of extraction and processing of mineral substances is one of the oldest occupations of mankind and has been over time the main driver of the development of human society. The world economy and implicitly the national economies are in a permanent hunger for resources, which must be satisfied either by exploiting their own deposits of mineral substances or by importing them. The mining industry has undergone great changes around the world over the past two decades.

After the cessation of non-ferrous metal ore mining activities in the late 1990s, there remained numerous mining sites in Romania that pose a risk to environmental components and indirectly to human health. The long-term negative effect on the environment has led to disruption of ecosystems and worsening living conditions in some areas.

Heavy metal pollution in former mining areas is an important environmental issue because the rehabilitation of these regions is partial or non-existent. The problem arises from several points of view: it reaches a large territory, does not stop at borders (cross-border pollution), is a global problem and requires a series of analyzes to accurately identify the risk (Doroțan et al., 2011).

This thesis deals with one of the former mining operations in northern Romania (EM Băiuț), which is part of the Baia Mare mining district (Costin et al., 2003) in the Eastern Carpathians and studies the impact on the environment, focusing on the middle and upper river basin of the Lăpuş River.

In terms of the quality of environmental factors, this thesis showcases the environmental degradation in the area and emphasizes the need for responsible policies in abandoned mining areas.

The **general objective** of the thesis is to assess the state of the environment in the middle and upper river basin of the Lăpuş River (Maramureș County) in terms of contamination of water, soil and sediments. The mining activity stopped at the end of the '90s in the Băiuț mining perimeter, leaving behind unfinished galleries, abandoned tailings ponds and concentrated ore remains. The acidic mine waters flow continuously and the ore particles with high concentrations in heavy, toxic metals are transported by the streams in the area that finally flow into the main watercourse, the Lăpuş River. These pollution sources certainly represent a threat to the Cheile Lăpușului Nature Reserve, which is located at a distance of 30 km from the Băiuț mining perimeter.

The **specific objectives** of the thesis are:

1) Literature review regarding the pollution in the upper and middle hydrographic basin of the Lăpuș River in relation with the Băiuț mining perimeter, by identifying the existing pollution sources.

2) Pollution assessment in terms of the source-carrier-receiver relationship.

3) Study on the variation of the concentration of heavy metals from upstream (E.M. Băiuț) to downstream (Cheile Lăpușului Natural Reserve) by analyzing water samples.

4) Study on the variation of physico-chemical parameters and the concentration of heavy metals in soil samples taken at different depths.

5) Determination of the concentration of dissolved major ions (SO_4^{2-}, Cl^-, NO^{2-}, NO^{3-} F^-, Br^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+, NH^{4+}) in the water samples and of the physico-chemical parameters (pH , ORP, EC, TDS, Sal) for water, soil and sediment samples.

6) Determination of the concentration of seven heavy metals (Fe, Pb, Cu, Zn, Ni, Cr, Cd) from the samples of surface water, mine water, soil and sediments.

7) Carrying out the granulometric analysis for soil and sediment samples and studying the relationship with the concentration of associated heavy metals.

8) Determining the quality of water, soil and sediments using specific quality indices.

The structure of the thesis is divided into two parts: the theoretical part in which the main theme is substantiated and the practical part where the personal contributions on the approached topic are presented.

The first part of the thesis consists of three chapters:

Chapter I - Mining and heavy metals, is a chapter where a documentary study was conducted on the issue of mining both nationally and internationally. Heavy metals associated with mining have been characterized in terms of their impact on water, soil and sediment quality.

Chapter II - Description of the study area. This chapter describes the study area considering its position in the river basin of the Lăpuș River as well as its position to the main source of pollution, E.M. Băiuţ. Data on natural conditions are presented: topography, geology, hydrography, climate, soils, vegetation, fauna and protected areas. The main sources of pollution are presented.

Chapter III - Materials and methods, are presented the stages of water, soil and sediment sampling and describes the methods used to obtain the data discussed in the second part of the thesis.

The second part of the thesis is structured in four chapters and represents personal contributions.

Chapter IV - Analysis of the parameters identified in the water samples - the results of the physico-chemical parameters of the studied surface water and mine water samples are presented: pH, electrical conductivity, redox potential, salinity, heavy metal content (Cd, Zn, Pb, Cu, Ni, Cr, Fe), anions (SO_4^{2-}, Cl^-, NO^{2-}, $NO^{3-}F^-$, Br^-) and cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+, NH^{4+}).

Chapter V - Analysis of the parameters identified in soil and sediment samples - presents the results of physico-chemical parameters (pH, electrical conductivity, redox potential, salinity, Cd, Zn, Pb, Cu, Ni, Cr, Fe) and the results of the granulometric analysis for the soil and sediments. The data obtained were used for the calculation of the parameters specific to the particle size distribution and for the Student test.

Chapter VI – Assessment of environment quality by using specific quality indices. In Chapter VI, based on the results obtained in Chapters IV and V, quality indices for water, soil and sediments were determined, with the help of which the state of the environmental components in the studied area was assessed.

Chapter VII - Conclusions, the last chapter presents the main conclusions regarding the experimental part, the results obtained from personal contributions as well as some future perspectives.

I. Mining and heavy metals

Mining is one of the earliest activities of mankind with ruins of mining sites dating back to the first period of the Stone Age. Depending on the use of metals, the periods in human history were also named, for example, the Iron Age and the Bronze Age (Pan et al., 2010). Even the oldest mining operations have resulted in the production of gaseous, liquid and solid waste. In historical times, mining waste has been released into the environment, some of it causing contamination or even pollution at local and regional level. Environmental pollution as a result of mining is not new in the industrialized world.

The raw materials provided by the mining industry are vital for almost all human activities and support various industries (ceramics, fossil fuels, construction, pharmaceuticals, jewelry and electronics) among many others (Azpagic, 2004). Without mineral resources, the industry would collapse and living standards would fall. Metal ores and coal are mined in large quantities, only for non-ferrous metals the total annual global production amounts to about 50x10^6 tons (Lottermoser, 2010).

Environmental issues related to past mining activities have become the subject of public interest only in the past 20-25 years (Alpers and Blowes, 1994; Jambor and Blowes, 1994; Plumlee and Logsdon, 1999; Filipek and Plumlee, 1999; Jambor et al., 2003). Consequently, the knowledge base related to the mitigation and control of environmental pollution in mining areas has seen a recent development.

Following the Revolution of 1989, the entire Romanian industrial system underwent a process of rapid restructuring by closing a large number of industrial units and inefficient facilities, including the mining sector (Marinescu et al., 2013). Mining operations were reduced from 278 in 1989 to 64 in 2009 (Lazăr, 2009). Due to the restructuring of the mining sector, the production of industrial minerals has decreased sharply or even stopped (Figure 1).

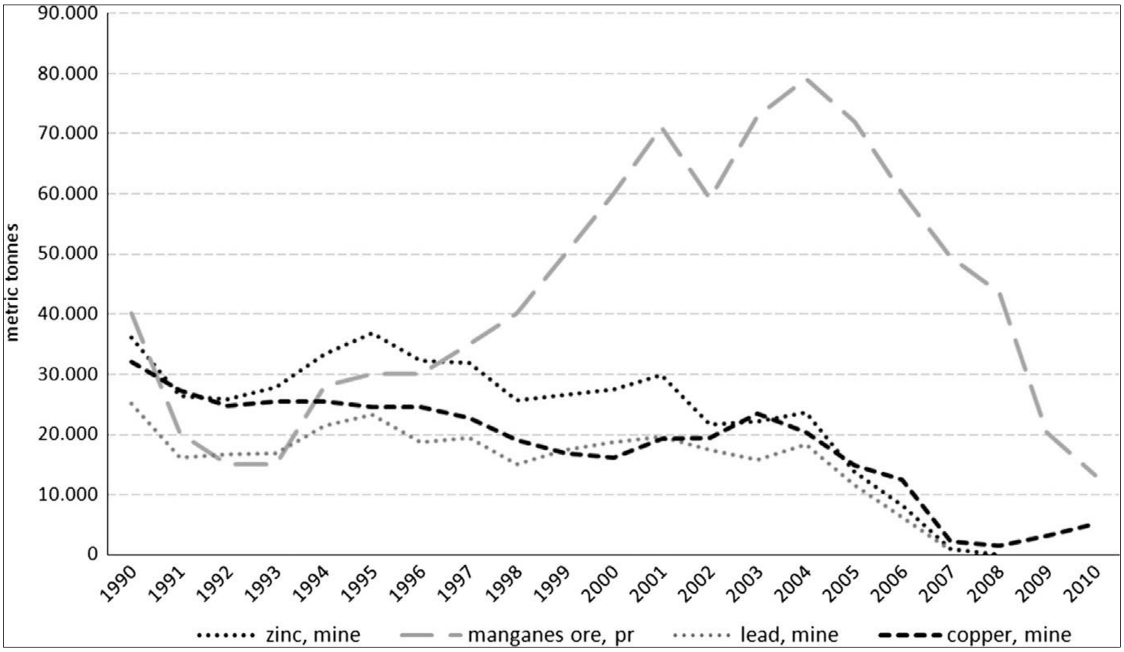


Figure 1. Production of metallic minerals from mining in Romania between 1990-2010, (Marinescu et al., 2013)

According to the 2017 inventory, Romania is the country with the highest percentage of waste from the extractive industry, over 85% of the total (the average in Europe is about 25%), most of which comes from historical mining (Ministry of Economy, 2017). According to the 2017 inventory regarding the situation of closed landfills on the territory of the European Union, out of the total of 3,462 closed landfills, 20% are on Romanian territory. There are a number of 627 tailings dumps and 68 tailings ponds belonging to the mining perimeters where the activity was stopped.

Heavy metals

Heavy metals are chemical elements that naturally belong to ecological systems (Greger, 2004), but have become pollutants with exploitation. This phenomenon has led to enrichment from anthropogenic sources such as mining, which far exceed the contributions from natural sources.

Heavy metals in water, soil and sediments

Historical and current mining activities have released large amounts of metal-bearing mineral particles into river systems (Lewin et al., 1977, 1983; Lewin and Macklin, 1987; Macklin et al., 1994; Hudson-Edwards et al., 1996, 1999, 2001; Miller, 1997).

Water pollution in mining areas is associated with the oxidation of weathered sulfur minerals (Figure 2). The result is effluents with a low pH and containing a high level of dissolved metals such as cadmium, copper, zinc, anions such as sulfates and carbonates plus suspended matter (Pentreath, 1994; Salomon, 1995).

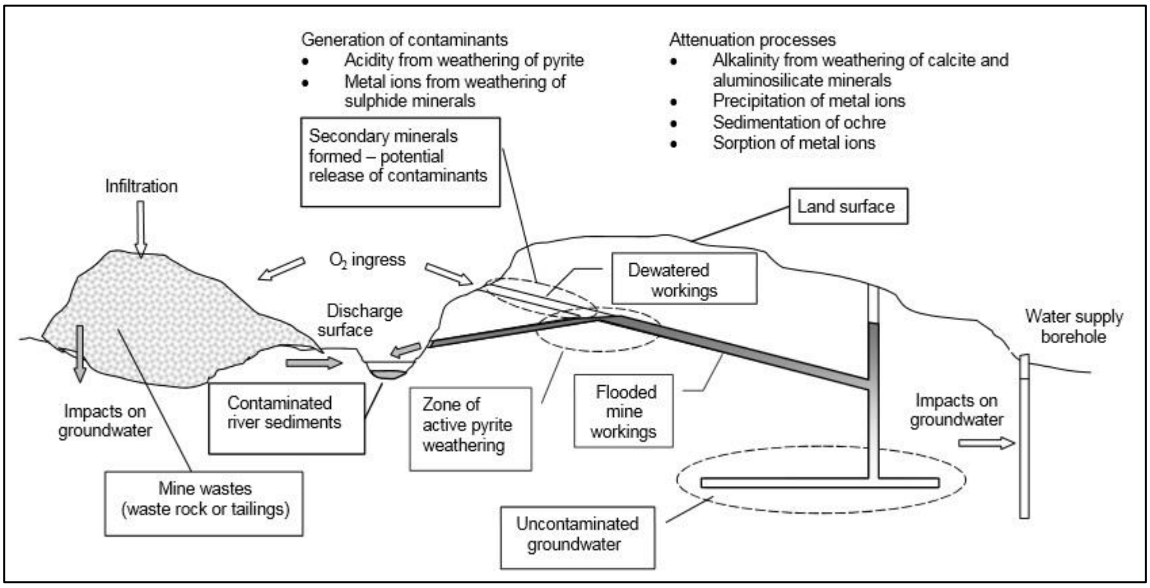


Figure 2. Main sources of pollution and propagation pathways in mining areas (image taken from Younger et al., 2002)

Many sedimentary systems function as excellent archives of past environmental changes, allowing us to take a look at the recent past. It also provides tools for monitoring changes in active sedimentary environments (Perry and Taylor, 2007). With the understanding of the sedimentation processes and the different resulting characteristics, the reconstruction of the environment can be done with much more certainty.

Sediments are increasingly recognized both as a carrier and as a possible source of contaminants in aquatic systems. These materials can also affect the quality of underground waters and of agricultural products when discharged directly into the field.

Contaminants are not permanently fixed by sediments. They can be recycled by biological and chemical agents both inside the sedimentary compartment and in the water column. Bioaccumulation and transfer in the food chain can be influenced by the proportions of pollutants associated with sediment. Benthic organisms have particular contact with sediments, thereforethe the level of contaminants in the sediment may have a greater impact on their wellbeing than the level of contaminants in the aquatic environment (Förstner, 1989).

Heavy metal contamination of different soil types has become an important environmental issue due to their nonbiodegradable nature and long half-life for their removal from the body (Wu and Zhang, 2010). The presence of these chemicals in the terrestrial environment poses a significant risk to the quality of soil, plants, natural waters and human health (Gowd et al., 2010). Heavy metals entering the soil remain present in the pedosphere for a long time even after the elimination of the pollution sources (Imperato et al., 2003). The major contaminants associated with mining areas are: As, Cd, Cu, Ni, Pb and Zn.

II. Description of the studied area

Recent studies indicate that one of the most polluted areas for the Lăpuş river basin is the Băiuţ mining perimeter (Macklin et al., 2003; Bird et al., 2003).

Knowing about this alarming situation, the present research aims to analyze the most threatened segment of this river by systematic testing, analyzing water, soil and sediment samples and comparing these values with the geochemical background of the area, national and international standards.

The studied region is located in the North-West of Romania, in the south of Maramureș County (Figure 3). The boundaries of the study area largely overlap with the boundaries of Lăpuș Country, respectively the upper and middle basin of the Lăpuș River.

The study area is drained by the Lăpuș River, which is the longest river in Maramureș County (114 km) and the almost unique water collector on the southern slopes of the volcanic mountains (Gutâi, Țibleș).

The water quality of the Lăpuș River is strongly influenced by the untreated wastewater and the industrial activity from the former non-ferrous ore processing units (E.M. Băiuț).

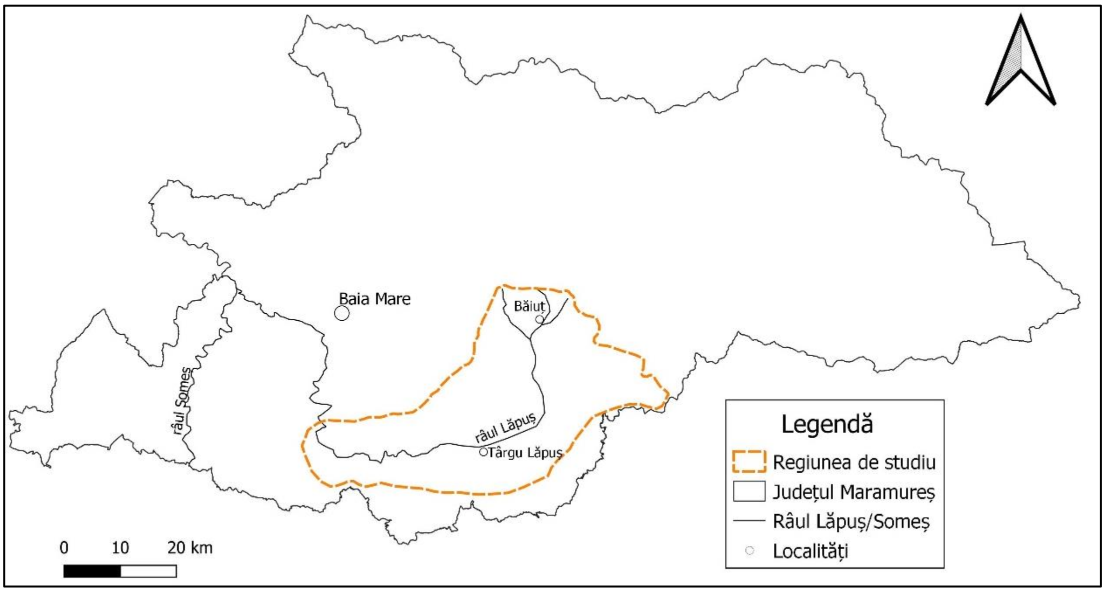


Figure 3. Location of the study area in Maramureș County

Regarding the geology, the study area belongs to the northern part of the Transylvanian Basin. The depression comprises a complex of geological units which belongs to three paleogeographic domains: the lens comprises the Preluca Massif, The Maramureș-Pannonian area and the Transylvanian area.

The Băiuț ore deposit is located approximately 45 km east of Baia Mare. Representing the eastern extremity of Baia Mare metallogenetic district, the Băiuț deposit is composed of the following three main ore deposits which from west to east are: i) Breiner-Băiuț, ii) Văratec şi iii) Cisma-Poiana Botizei.

In Băiuţ–Poiana Botizei Area, the hydrothermal mineralization and the ore accumulations tied to the Neogene magmatic activity were studied by Dimitrescu and Gheorghiţă (1962), Pomârleanu et al. (1968); Manilici and Kalmár (1973), Achim and Cioltea (1991), Valdman (1996), Chioreanu and Fülöp (2000). The mineralizations were integrated in the Baia Mare metallogenetic district (Borcoş et al., 1976; Mariaş, 2005).

Lăpuș Country is distinguished by a morphologically varied relief, from volcanic mountain massifs, such as the Țibleș Mountains, Lăpuș Mountains to golf depressions that pierce the volcanic mountain massifs: Lăpușului depression, Poiana Botizii, Băiuț, Bloaja and Cavnic . In the relief of Lăpușului Country there are especially notable forms such as:

island mountains (Preluca Massif) formed by crystalline schists, terraces and proluvio-alluvial lowland depressions, Lăpuș Gorge, Șatra Mountain.

The study area is characterized by a temperate continental climate of transition, with differences between the eastern and western parts. The mountainous region in the eastern part is under the influence of subpolar air masses, while in the western part a moderate continental climate with oceanic influences predominates.

The average temperature for the last 6 years at the meteorological station Târgu Lăpuș is 9.7°C. Precipitations are between 700 and 1200 mm annually. The average number of rainy days per year reaches 140, and 30 day with snow (Retegan et al., 1980).

The Lăpuș River is almost the unique collector of the southern slopes of the Gutâi-Țibleș Volcanic Mountains and of the Lăpuș Mountains, with a strong right asymmetry (Figure 4). It is the longest river in Maramureș County (Posea et al., 1980). On the territory of the Lăpuș basin, a number of 210 tailings dumps with a storage capacity of 3.929.676 cubic meters of material were identified (Kalmár, 2000).

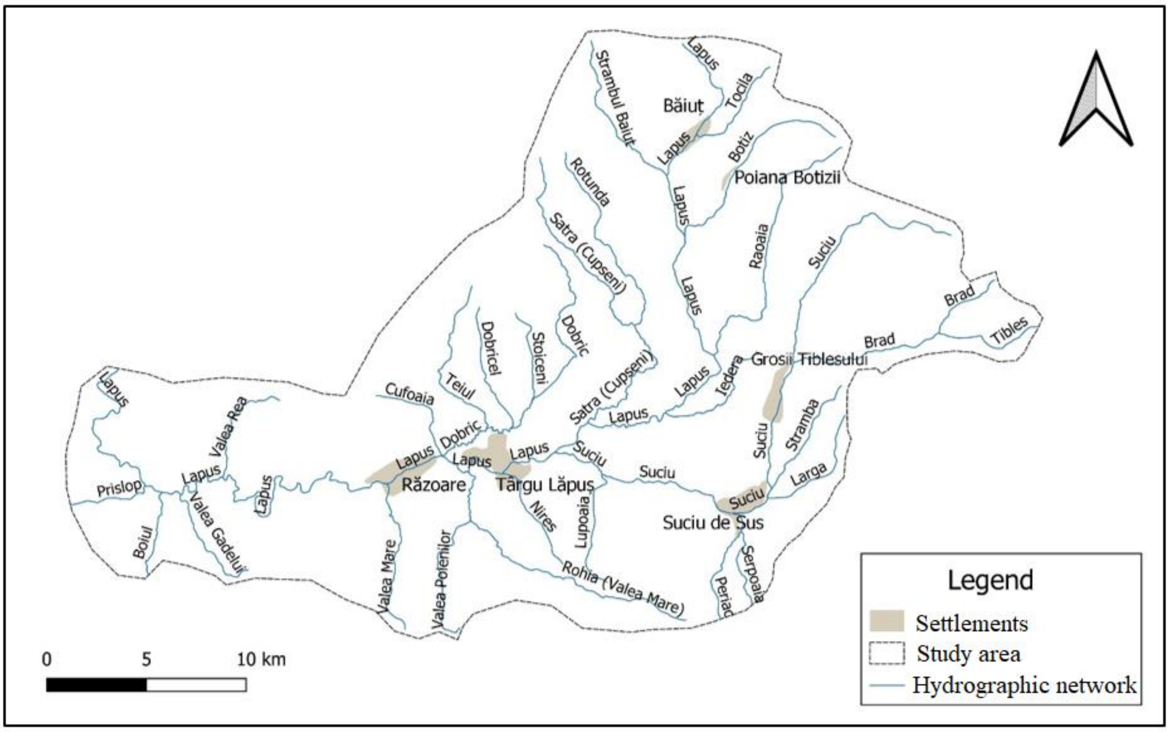


Figure 4. River basin in the studied region

The Băiuț mining perimeter is located 30 km northeast of the city of Târgu Lăpuș and 80 km southeast of Baia Mare, it is a specific mining area, the commune being located on a valley delimited by high mountains. The commune is delimited in three lateral parts: Băiuț

- the commune's residence, Strâmbu Băiuț village and Poiana Botizii village, it covers a distance between 2 km Strâmbu Băiuț and 12 km Poiana Botizii.

The study area includes the following mining objectives:

Breiner mine

The Breiner mine is located at approx. 1 km northeast of Băiuţ commune, between Valea Capra and Izvorul Alb, with access on an unmodernized road on Valea Conciului. The entrance to the mine was through the Hell gallery shown in the image below (Figure 5).

Figure 5. Entering the Breiner mine. (Doroțan Dora, May 2020)

The mine closed in 2006 and flooded the well. The mine waters are gravitationally evacuated with a flow rate of 7.5 l/s. To neutralize mine water, a quantity of 78 t/month of lime is required, taking into account a specific lime consumption of 4g/l (Remin S.A., 2016).

Văratec mine

The dome of the Văratec transversal gallery it is the largest landfill in the area, totaling 767.250 m^3 of material: andesites, pyritized andesitic breccias, sandstones, partially ferrous oxidized sulfur ore as well as waste of all kinds, concrete and rubble (Kalmár, 2000).

The mine closed in 2006 and it was ordered to remove the pumps and flood the well. The strong acid mine water was discharged through concrete pipes in the Tocila valley to be treated under natural conditions. At present, the water does not come out of the mine, it is collected in the 300 m deep well. Thus, the Văratec mine does not produce surface water pollution at present times.

Bloaja tailings pond

The active Bloaja pond (Figure 6) is a valley-type pond, with two dams (upstream and downstream), built by damming the Bloaja valley, which is channeled. It became operational in 1975. It has a length of 525 m, an average width of 217 m and a capacity of approximately 1,750,000 m^3 (Kalmár, 2000).

Figure 6. Bloaja tailings pond (Doroțan Dora, May 2020)

III. Material and methods

The sampling points were chosen according to the areas that represent a possible source of pollution, but at the same time samples were collected from areas where there was no mining activity (Libotin and Dobric). The streams related to these villages are outside the mining perimeter and have the role of reference streams, the pollution from those sectors can be attributed to the geochemical background of the substrate, with small influences due to domestic activities.

A total of 45 water samples were taken, of which 8 for mine water and 37 for surface water. Out of the total of 45 samples, 10 samples were taken from the main course of the Lăpuș River, and the rest from its tributaries (Table 5). The water samples were collected in June 2014, and their numbering started from the number 6, taking into account the fact that the samples taken during the author's master thesis were numbered from 1-5.

The samples were collected from various key points: in the vicinity of mining perimeters, tailings dumps and tailings ponds, in areas where there were exploration and geological prospecting activities (Poiana Botizii) and upstream and downstream of confluence points.

Soil and sediment samples were taken from the same points as water samples, both from mining areas and adjacent sites. The soil and sediment samples were collected in April 2014.

The sediment samples (stream sediment) were taken from the mobile alluviums of the river, mostly from the sand and totalled 27 in number. This sand also contains fragments of sulfides, especially from the tailings ponds and subordinate, from the deposit.

The soil samples were collected from a depth of 0-40 cm and 40-90 cm from the agricultural lands near the studied hydrographic network with a total of 26 samples. The amount of sample collected was 150-500 grams each. Sampling points were located based on GPS coordinates using the Garmin Etrex GPS

Physico-chemical parameters of the water samples were determined using a WTW INOLAB 320i portable multiparameter. For this, the water samples were taken to the laboratory within 48 hours from the time of sampling, being kept at a temperature of 4ºC. Parameters were determined such as:

- Temperature (t)
- pH
- Oxidation-reduction potential (ORP)
- Electrical conductivity (EC)
- Total dissolved solids (TDS)
- Salinity (Sal)

To determine the content of dissolved major ions, water was taken in two vials. The samples were filtered through a filter having a porosity of 0.45 µm. To determine the cations, the water samples were acidified to a pH of about 3 using 65% HNO3. The electrical conductivity of the water samples was brought to a value of 100 µS/cm using ultrapure water (0.055 µS/cm; 18.2 MΩ/cm). The ultrapure water was purified using the Ultra Clean TWF UV system (SG GmbH, Germany). The laboratory glassware was previously washed with distilled water and ultrapure water. The content of dissolved majority ions was determined using ion chromatograph IC 1500 DIONEX 2015 respecting the conditions in the related operating manual.

The heavy metals content (Pb, Fe, Zn, Ni, Cd, Cu, Cr) was determined using the ZEEnit 700 Analytic Jena atomic absorption spectrometer with air-acetylene (C2H2-air) flame and graphite furnace with platform and cathode lamp cavity corresponding to each metal, respecting the operating conditions in the corresponding manual (Figure 20). Previously, the water samples were filtered through a filter having a porosity of 0.45 µm, then acidified to a pH of less than 2 using 65% HNO_3. The pre-processed sample is aspirated and introduced into the apparatus by means of a special device, and the concentration of heavy metals was expressed in mg/L.

The granulometric analysis of the soil and sediment samples was performed according to STAS 1913 / 5-1985 (sieving method) and SR EN 14688-2: 2005 (sedimentation method).

IV. Analysis of the parameters idetified in water samples

Water samples were taken from the Lăpuș River and its tributaries, from areas where the existence of mining pollution is known (former mining galleries, tailings pond), areas where only research and prospecting activities were carried out (Poiana Botizii) but also outside the areas mining in order to have reference values.

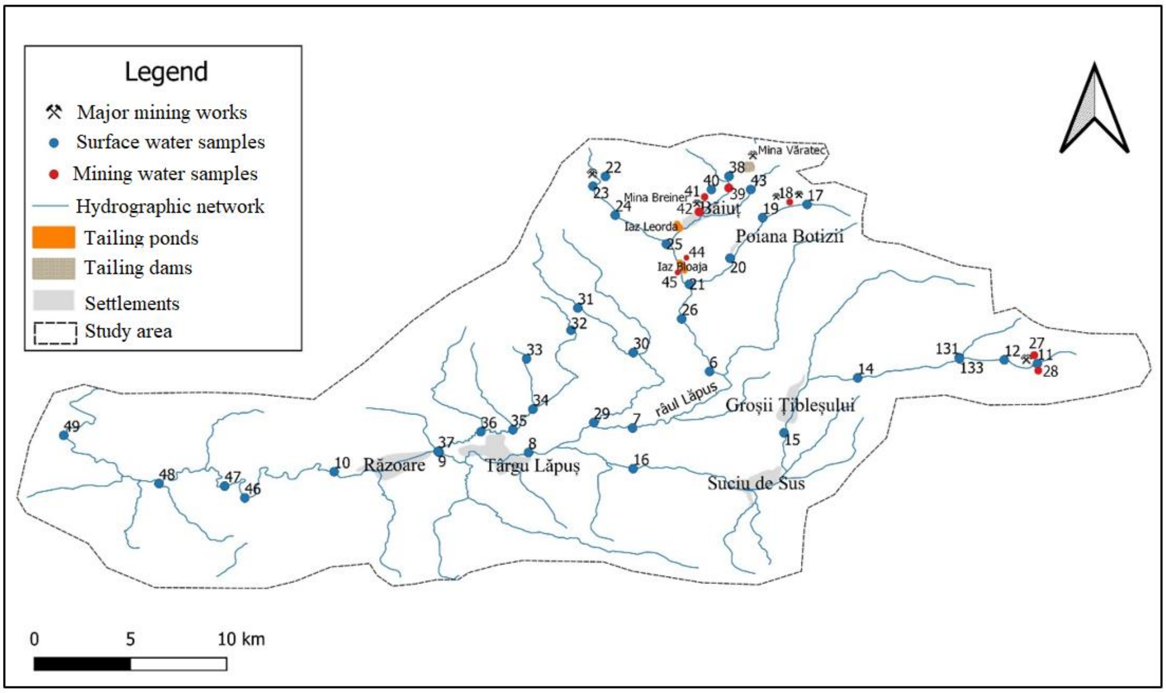


Figure 7. Water sampling points

Table 1 presents a synthesis of the physico-chemical parameters identified in the surface water samples taken (Figure 8).

Table 1. Statistical data on the values of physico-chemical parameters for surface water samples (37 samples)

Parameter	Minimum	Maximum	Average	Median	Standard deviation
pH	5.43	7.80	7.35	7.50	0.50
ORP (mV)	-48.00	72.30	-23.59	-29.20	23.64
EC (µS/cm)	26.00	376.00	180.13	165.00	88.18
TDS (mg/L)	31.00	241.00	116.16	107.00	55.45
Salinitate (‰)	0.00	0.10	0.01	0.00	0.03

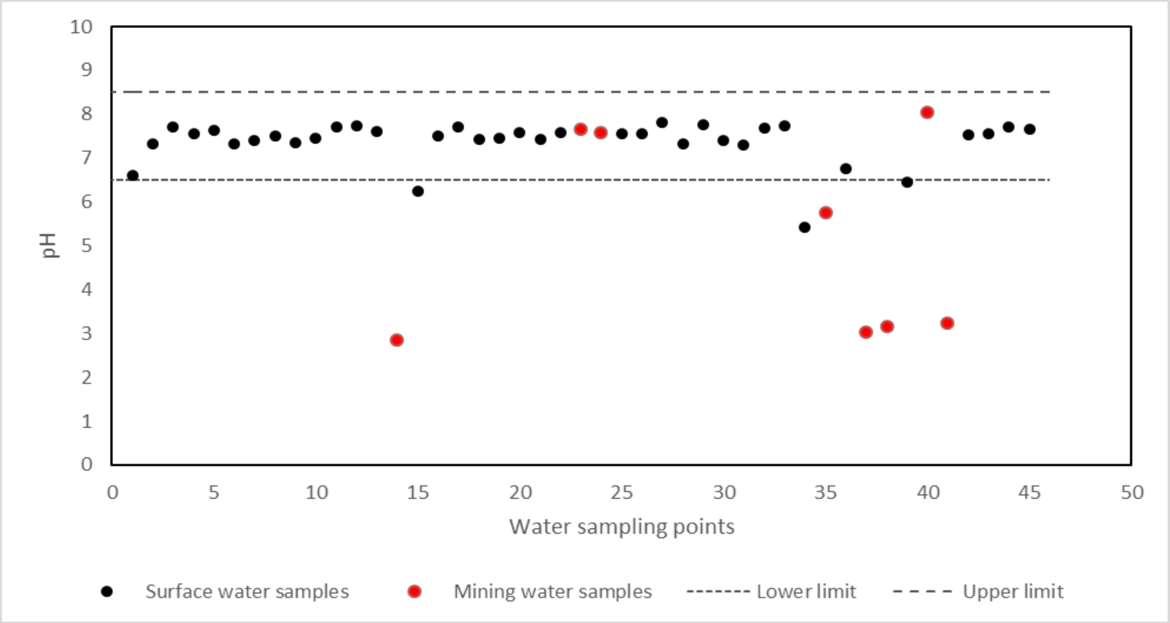


Figure 8. pH variation in the studied water samples

The pH of the surface water samples varied between 5.43 (sample 38) and 7.80 (sample 31), indicating an acidic to basic character (Figure 8). Three surface water samples had values lower than the lower limit, imposed by legislation (Order 161/2006). The lowest pH value, identified in sample number 38 is due to the natural geochemical background of the area, which determines an acidic character of the water. The sample was taken upstream from the Văratec mine, from Izvorul Alb, which through the erosion of the ores of the geological substrate receives a naturally acid character. It is expected that in areas characterized by metal-bearing formations, these metals will appear, at high levels and outside the exploited mining perimeters (Förstner, 1989).

Table 2 presents a synthesis of physico-chemical parameters in the studied mine water samples.

Table 2. Statistical data on the values of physico-chemical parameters for mine water samples (8 samples)

Parameter	Minimum	Maximum	Average	Median	Standard deviation
pH	2.84	8.05	5.17	4.50	2.19
ORP (mV)	-78.70	240.90	92.34	121.75	122.32
EC (µS/cm)	2.57	7090.00	1997.62	497.00	2455.52
TDS (mg/L)	84.00	4537.60	1485.35	1015.50	1496.06
Salinitate (‰)	0.00	3.80	1.16	0.75	1.30

The pH of the mine water samples had values between 2.84 (sample 18) and 8.05 (sample 44) causing the water to be very acidic towards the base (Figure 8). Out of the total, 5 samples had values below the lower limit imposed by law (H.G. 352/2005). Sample 18 was taken from the entrance to a former mining gallery, Gallery 8, Bear's Coast from Poiana Botizii, and sample number 44 from the former Bloaja tailings pond. Low pH values lead to increased solubility and mobility of metals and increased risk of metal contamination in nearby watercourses, groundwater and agricultural land (Ozunu et al., 2009; Modoi et al., 2014).

As can be seen in Table 3, chloride (Cl^-), sulfate (SO_4^{2-}), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions were identified in all surface water samples. They were followed by nitrate ion, fluoride and lithium ion. The nitrate and phosphate ion was identified in a single sample, and the ammonium and bromide ion had values below the detection limit. Bromide and ammonium ion were not identified in the studied water samples.

Table 3. Data on the concentration of dissolved major ions in surface water samples

Parameter	Minimum	Maximum	Average	Median	Standard deviation
Li^+ (mg/L)	0.03	0.09	0.05	0.03	0.03
Na^+ (mg/L)	1.23	16.59	7.34	7.32	3.71
K^+ (mg/L)	1.01	14.55	4.50	4.08	2.68
Mg^{2+} (mg/L)	0.88	15.18	6.08	6.03	3.62
Ca^{2+} (mg/L)	4.74	76.94	29.28	28.74	16.94
Cl^- (mg/L)	0.60	20.28	6.22	5.35	3.59
F^- (mg/L)	0.10	8.74	0.57	0.32	1.43
NO_3^- (mg/L)	0.70	15.12	5.88	5.12	3.36
SO_4^{2-} (mg/L)	11.36	151.58	49.54	35.10	34.63
PO_4^{3-} (mg/L)	4.21 (38)				
NO_2^- (mg/L)	1.38 (31)				
Br^- (mg/L)	SLD				
NH_4^+ (mg/L)	SLD				

The order of the concentration of the majority ions present in the studied mining water samples was: $SO_4^{2-} > Ca^{2+} > Mg^{2+} > Na^+ > K^+ > Cl^- > NO_3^- > F^- > Li^+$ (Table 4). Lithium ion was identified in only one sample (18).

Table 4. Statistical data on the concentration of dissolved majority ions in mine water samples

Parameter	Minimum	Maximum	Average	Median	Standard deviation
Cl^- (mg/L)	0.96	7.68	3.93	4.44	2.33
F^- (mg/L)	0.36	0.59	0.51	0.59	0.11
SO_4^{2-} (mg/L)	31.66	7598.40	1517.17	144.30	2447.18
NO_3^- (mg/L)	0.62	5.58	2.95	3.15	1.89
Na^+ (mg/L)	3.53	35.89	17.82	14.73	12.55
K^+ (mg/L)	2.12	33.16	11.88	8.43	10.69
Mg^{2+} (mg/L)	2.76	226.55	85.82	59.62	83.81
Ca^{2+} (mg/L)	24.02	292.96	104.76	72.14	91.61
Li^+ (mg/L)	0.64 (18)				
NH_4^+ (mg/L)	SLD				
PO_4^{3-} (mg/L)	SLD				
Br^- (mg/L)	SLD				
NO_2^- (mg/L)	SLD				

Among anions, sulfate ion (SO_4^{2-}) is predominant in both surface and mine waters. The values of this ion are between 11.36 mg/L and 151.58 mg/L (average 49.54 mg/L) in surface waters and between 31.66 mg/L and 7598.40 mg/L (average 1517.17 mg/L) in mine waters.

Of the seven heavy metals analyzed, only five were identified in surface water samples in the following percentages: Fe(100%), Cu(92%), Zn(81%), Pb(73%) and Cr(5%). Cadmium and nickel were below the detection limit of the spectrometer. (Table 5).

Copper registered the largest variations of the concentration in the surface water samples, the values being between 6.53 µg/L and 942.90 µg/L being followed by zinc with values between 1.54 µg/L and 471.50 µg/L.

Table 5. Statistics on the concentration of heavy metals in surface water samples (37 samples)

Parameter	Minimum	Maximum	Average	Median	Standard deviation
Fe (mg/L)	0.04	3.64	0.91	0.73	0.86
Cu (µg/L)	6.53	942.90	78.72	26.56	161.88
Zn (µg/L)	1.54	471.50	125.35	75.40	136.25
Pb (µg/L)	3.03	70.50	17.69	11.50	15.30
Cr (µg/L)	3.80	7.69	5.75	5.75	1.95
Ni (µg/L)	0.00	0.00	0.00	0.00	0.00
Cd (µg/L)	0.00	0.00	0.00	0.00	0.00

The order of the concentration of heavy metals in the case of mining waters was: Zn> Fe> Cu> Ni> Cd> Cr> Pb (Table 6).

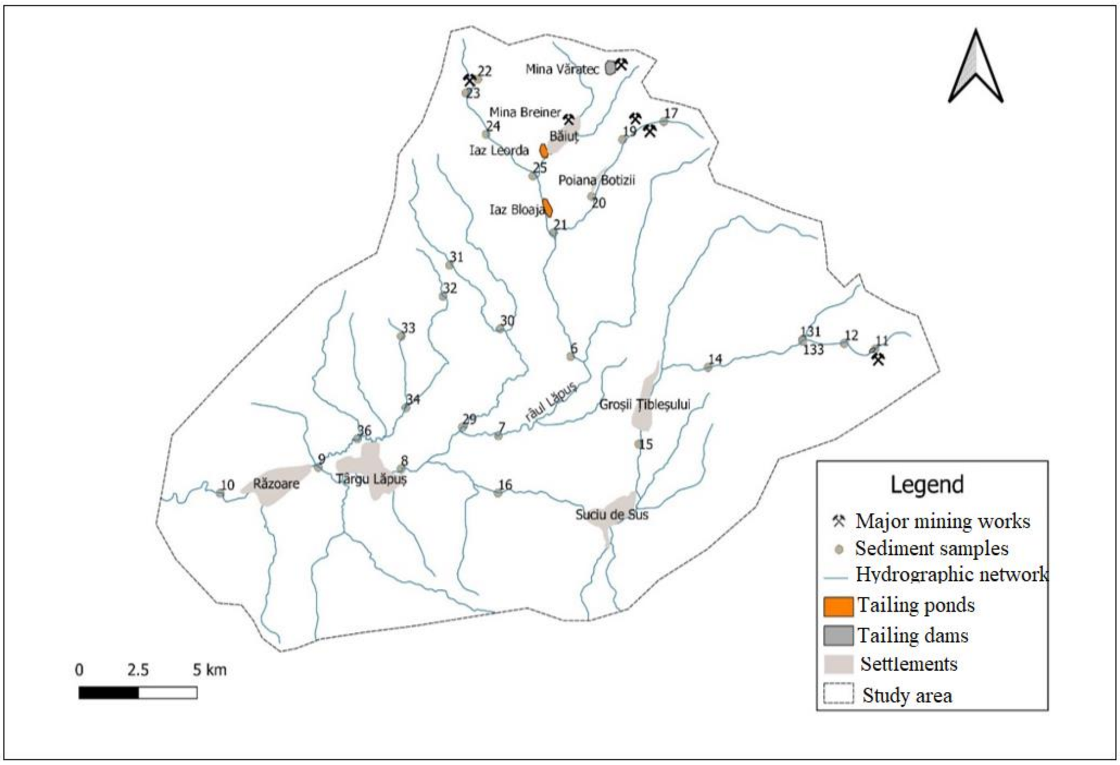
The dominant heavy metal was zinc with concentrations between 8.9 µg/L and 60.931 µg/L, its average (19.407 µg/L) exceeding 38 times the maximum permitted concentration (500 µg/L) required by law (H.G. 352/2005).

Table 6. Statistics on the concentration of heavy metals in mine water samples (8 samples)

Parameter	Minimum	Maximum	Average	Median	Standard deviation
Fe (mg/L)	0.02	34.93	15.86	11.86	15.75
Zn (µg/L)	8.90	60931.00	19407.22	5853.00	22868.25
Cu (µg/L)	7.93	23904.00	6075.92	1636.45	8383.26
Ni (µg/L)	14.00	4097.00	1352.31	734.70	1452.40
Pb (µg/L)	5.80	113.00	31.78	12.00	41.03
Cr (µg/L)	7.95	267.30	78.36	41.20	95.68
Cd (µg/L)	21.40	877.90	308.88	101.30	327.53

V. Analysis of the parameters identified in the soil and sediment samples

The sediment samples were taken from the same points as the water samples being represented by the mobile alluviums of the river.



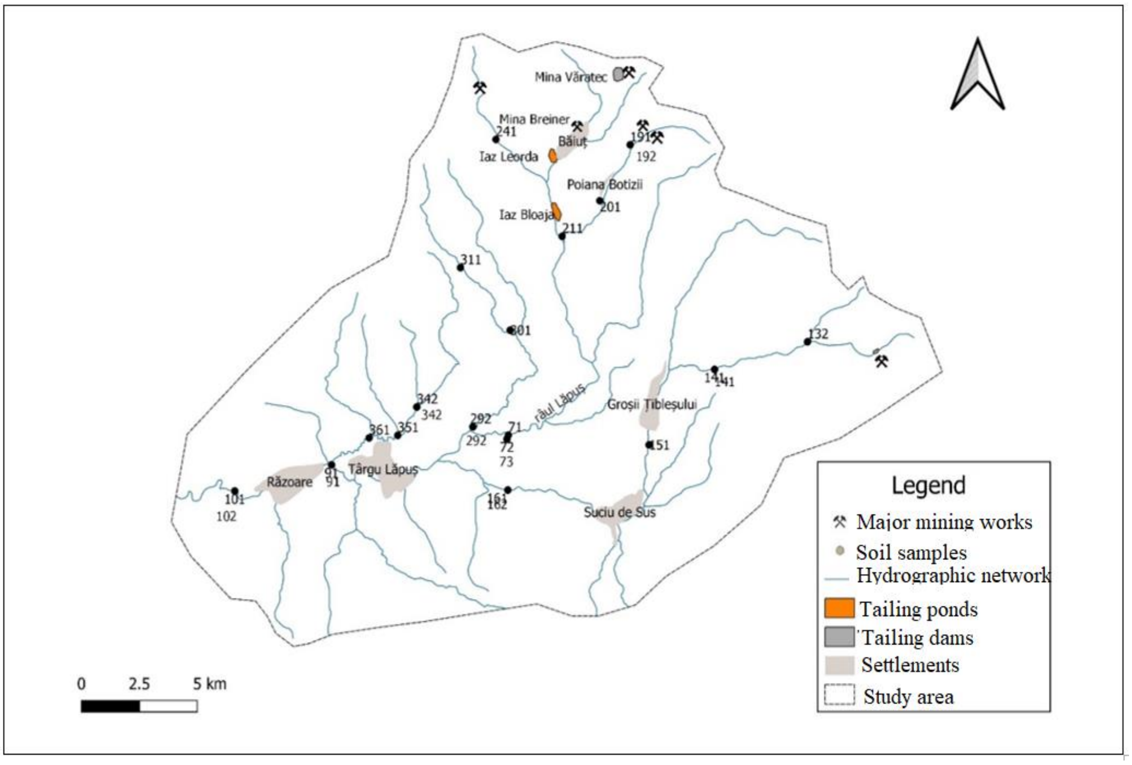


Figure 9. Soil and sediment sampling points

Soil samples were taken in the vicinity of water and sediment samples, respectively from the agricultural land located along the Lăpuș river and its tributaries.

Table 7 and Table 8 present a synthesis of the physico-chemical parameters identified in the soil and sediment samples (Figure 9).

Table 7. Statistical data on the values of physico-chemical parameters of sediment samples (27 samples)

Parameter	Minimum	Maximum	Average	Median	Standard deviation
pH	6,57	7,91	7,27	7,29	0,35
ORP (mV)	-56,4	21,5	-18.24	-18,7	19,28
EC (µS/cm)	26,00	581	101,64	77,90	105,82
Salinitate (‰)	0,00	0,2	0,01	0,00	0,04

Table 8. Statistical data on the values of physico-chemical parameters of soil samples (26 samples)

Parameter	Miniumum	Maximum	Average	Median	Standard deviation
pH	5,16	7,84	6,79	6,87	0,70
ORP (mV)	-49,10	107,30	10,94	6,60	39,50
EC (µS/cm)	4,40	441,00	62,62	40,05	83,05
Salinitate (‰)	0,00	0,00	0,00	0,00	0,00

The pH values of the soil samples varied between 5.16 and 7.84, which determines the reaction of the soil as moderately acidic to weakly alkaline. The retention of heavy metals in the soil depends on factors such as the nature of the mineral and organic components, the origin of the metals, the soil composition, pH and EC (Șipoș, 2010). The pH values of the sediment samples were between 6.57 and 7.91, most of the samples can be classified as weakly alkaline.

A summary of the concentration of heavy metals identified in the soil and sediment samples is presented in Table 9 and Table 10.

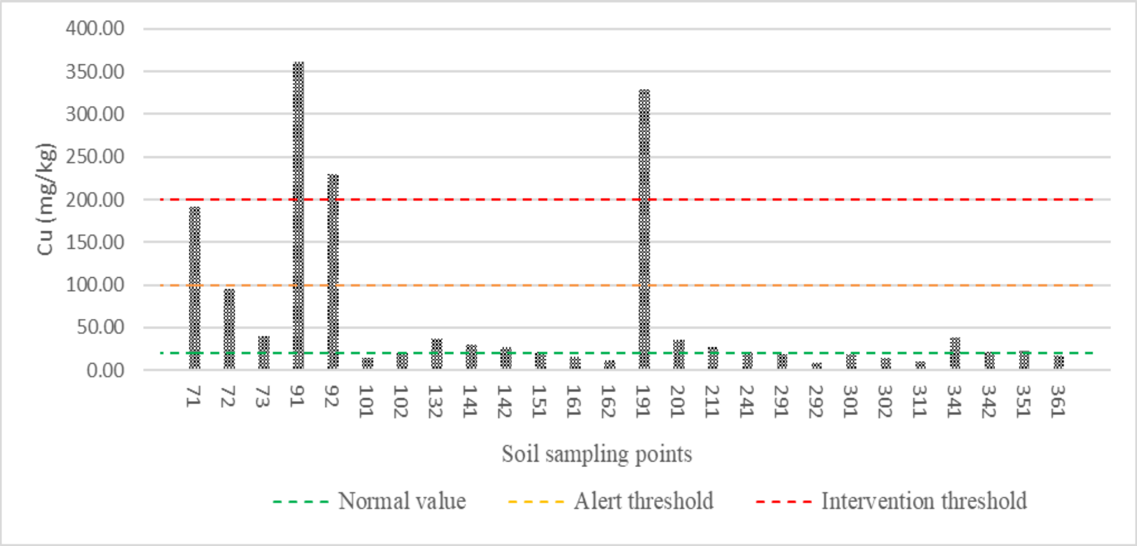
Table 9. Statistics on the concentration of heavy metals in soil samples (26 samples)

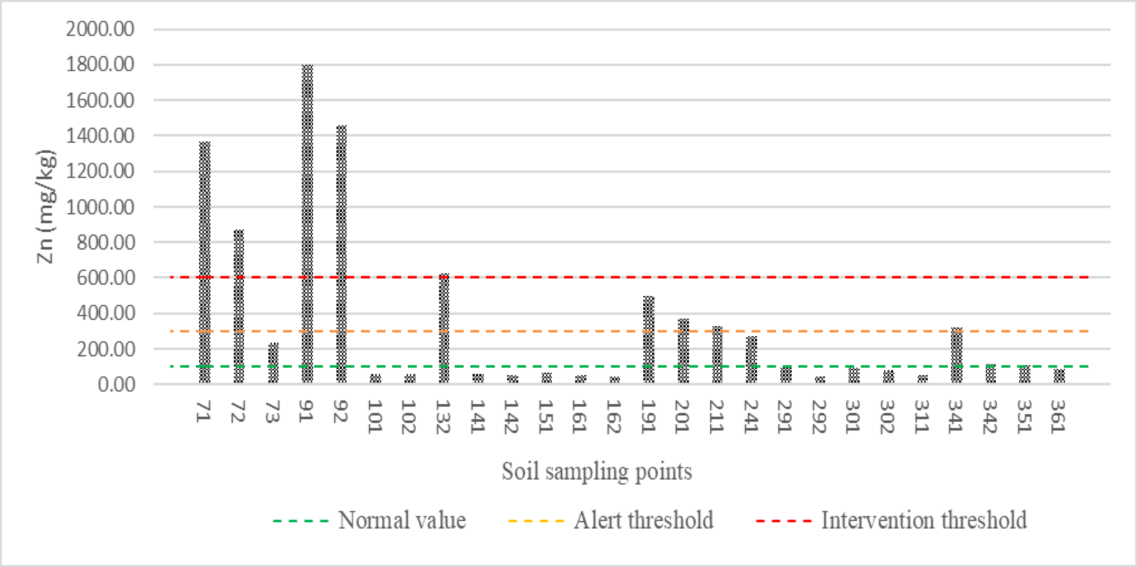
Parameter	**Minimum**	**Maximum**	**Average**	**Median**	**Standard deviation**
Cu (mg/kg)	8.27	361.00	64.58	22.42	96.19
Ni(mg/kg)	19.34	83.93	36.17	33.90	14.62
Zn(mg/kg)	43.77	1796.80	354.10	102.25	477.53
Cd(mg/kg)	0.31	5.24	1.59	1.21	1.13
Pb(mg/kg)	12.17	498.00	86.97	34.88	122.09
Cr(mg/kg)	2.39	40.80	15.93	14.18	8.48
Fe(mg/kg)	99661.57	116932.54	108069.36	107538.35	6985.65

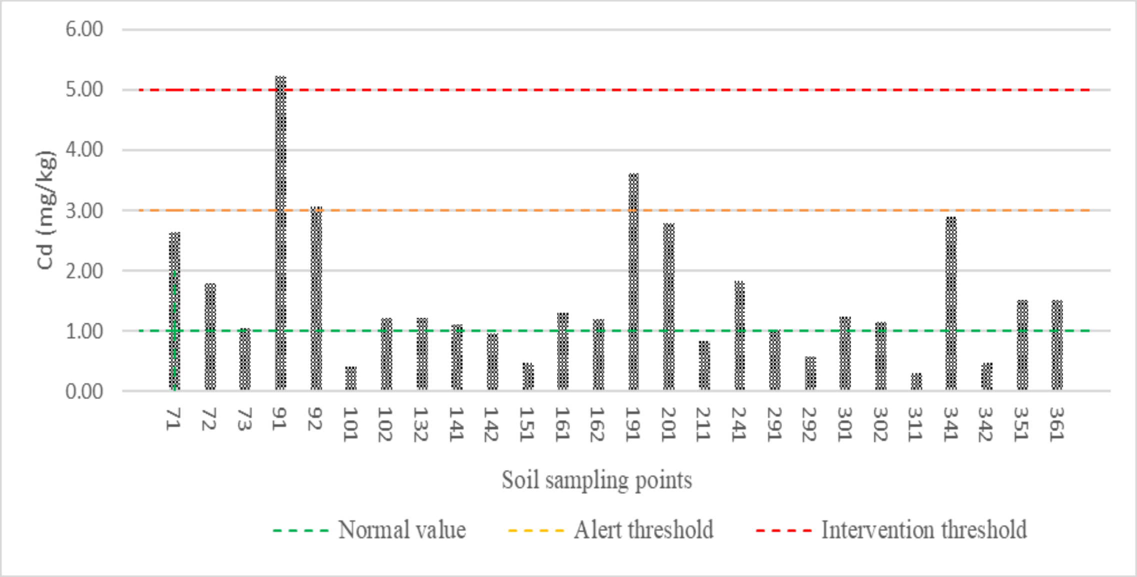
The results on the concentration of heavy metals in the soil samples indicate large ranges of values depending on the sampling point. The order of concentration of heavy metals in the soil samples was: Fe> Zn> Pb> Cu> Ni> Cr> Cd (Table 9).

The highest values were registered in the case of iron where concentrations were between 99.661,57 mg/kg and 116.932,54 mg/kg, the average was 108.069,36 mg/kg. The high concentrations represent the geochemical background of the soil in the region, in the soil iron being one of the basic elements.

The second dominant element was zinc with values between 43.77 mg/kg and 1.796,80 mg/kg, with an average value of 354.10 mg/kg exceeding 3 times the normal level of zinc in the soil. Of the total samples, 15% exceeded the alert threshold level (100 mg/kg) and 19% exceeded the intervention threshold level (300 mg/kg) (Figure 10).


400.00
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
Cu (mg/kg)
71
72
73
91
92
101
102
132
141
142
151
161
162
191
201
211
241
291
292
301
302
311
341
342
351
361
Soil sampling points
Normal value
Alert threshold
Intervention threshold


2000.00
1800.00
1600.00
1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
Zn (mg/kg)
71
72
73
91
92
101
102
132
141
142
151
161
162
191
201
211
241
291
292
301
302
311
341
342
351
361
Soil sampling points
Normal value
Alert threshold
Intervention threshold


6.00
5.00
4.00
3.00
2.00
1.00
0.00
Cd (mg/kg)
71
72
73
91
92
101
102
132
141
142
151
161
162
191
201
211
241
291
292
301
302
311
341
342
351
361
Soil sampling points
Normal value
Alert threshold
Intervention threshold

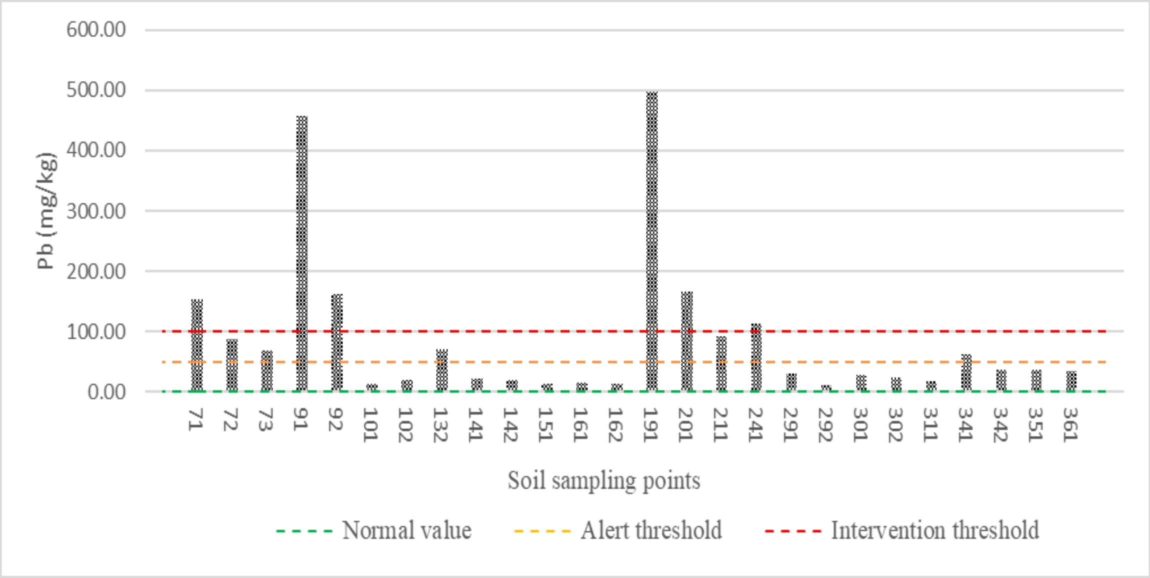


Figure 10. Variation of the concentration of heavy metals in the studied soil samples

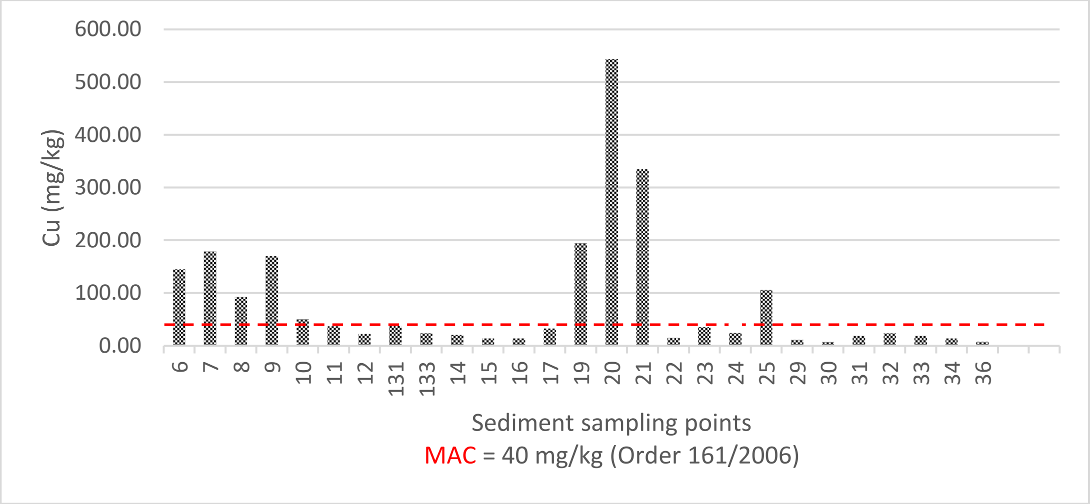
The highest values of the concentration of heavy metals in the soil samples were recorded in samples 71-72 and 91-92. These areas are located along the course of the Lăpuș River and are under the influence of the load of heavy metals from the former mining perimeter of Băiuț. Both sectors are upstream of confluence points, and high concentrations of heavy metals can also be the result of rising water levels, at which point heavier particles settle along the sand.

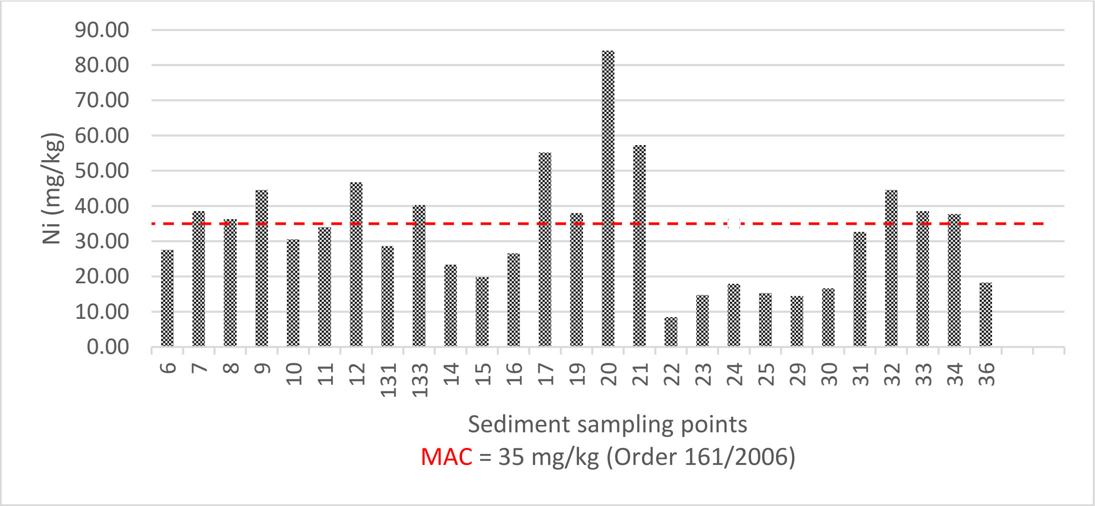
The order of concentration of heavy metals in the sediment samples was Fe> Zn> Cu> Pb> Ni> Cr> Cd (Table 10).

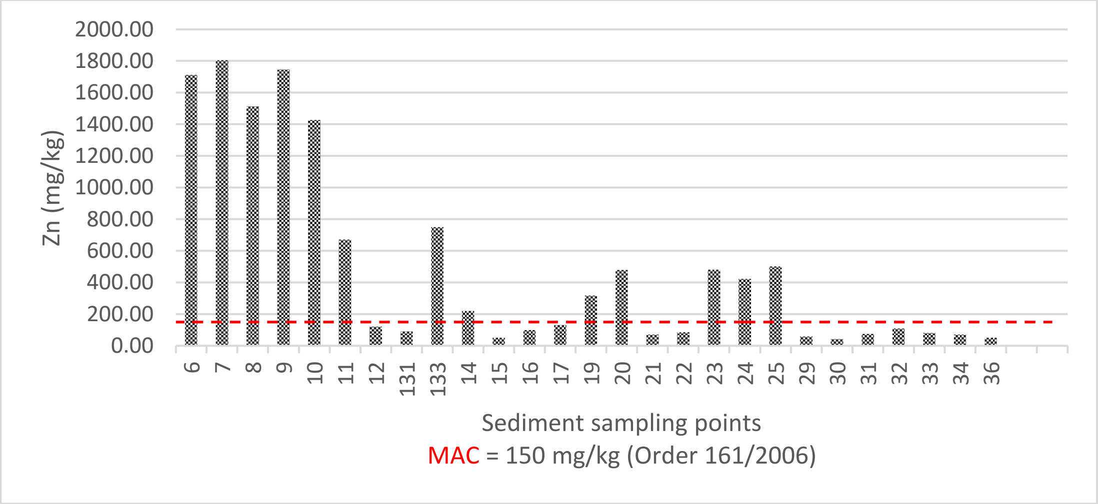
Table 10. Statistical data on the concentration of heavy metals in sediment samples (27 samples)

Parameter	Minimum	Maximum	Average	Median	Standard deviation
Cu (mg/kg)	7.43	543.67	81.36	24.16	118.76
Ni(mg/kg)	8.49	84.17	33.01	32.62	16.10
Zn(mg/kg)	42.27	1805.80	488.36	130.60	586.59
Cd(mg/kg)	0.60	3.68	1.92	1.70	0.93
Pb(mg/kg)	12.37	363.33	62.97	39.50	67.49
Cr(mg/kg)	2.27	20.30	10.46	10.04	4.93
Fe(mg/kg)	99187.89	117404.75	106357.75	101698.37	6903.39

In terms of exceeding the maximum permitted concentration, 89% of the sediment samples exceeded the limit for cadmium, 48% for zinc, 44% for nickel, 33% for copper and 22% for lead. In the case of chromium, there were no exceedances of the maximum allowed concentration (Order 161/2006) (Figure 11).


600.00
500.00
400.00
300.00
200.00
100.00
0.00
Cu (mg/kg)
6 7 8 9 10 11 12 131 133 14 15 16 17 19 20 21 22 23 24 25 29 30 31 32 33 34 36
Sediment sampling points
MAC = 40 mg/kg (Order 161/2006)


90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Ni (mg/kg)
6 7 8 9 10 11 12 131 133 14 15 16 17 19 20 21 22 23 24 25 29 30 31 32 33 34 36
Sediment sampling points
MAC = 35 mg/kg (Order 161/2006)


2000.00
1800.00
1600.00
1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
Zn (mg/kg)
6 7 8 9 10 11 12 131 133 14 15 16 17 19 20 21 22 23 24 25 29 30 31 32 33 34 36
Sediment sampling points
MAC = 150 mg/kg (Order 161/2006)

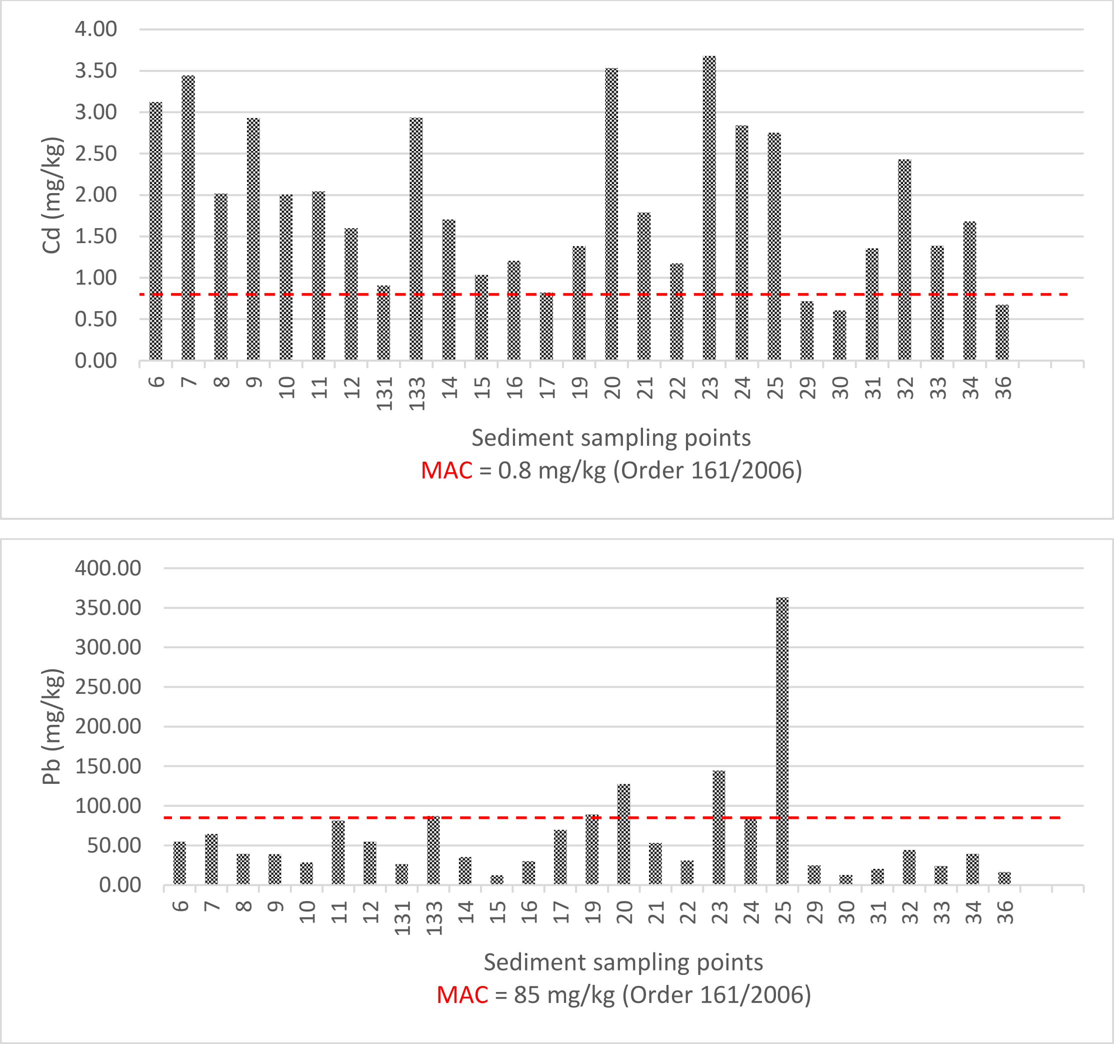


Figure 11. Variation of heavy metal concentration in the studied sediment samples

The highest values were recorded in sediment samples number 6, 7, 8, 9, 10, on the section Lăpușul Românesc - Cheile Lăpușului nature reserve. This may be due to the contribution of toxic metals deposited over time, Lăpuș being the main watercourse that receives acidic waters from the former Băiuț mining perimeter. There is an increase in the concentration of heavy metals in sediment sample number 20 (Cu and Zn) and in samples 23, 24 (Zn). This is due to the discharge of acidic water from the former mining galleries in these mountain streams.

Particle size distribution

In most of the sediment and soil samples, the sand content exceeds 75%, which includes these samples in the category of sands. The texture of the sediment samples is represented mainly by sands, 70% of the samples have sand as the predominant fraction, 12% gravel, 11% clay and 7% silt. The texture of the soil samples is mainly represented by sands, 70% of the samples have as predominant fraction sand, 15% silt and 15% clay (Figure 12).

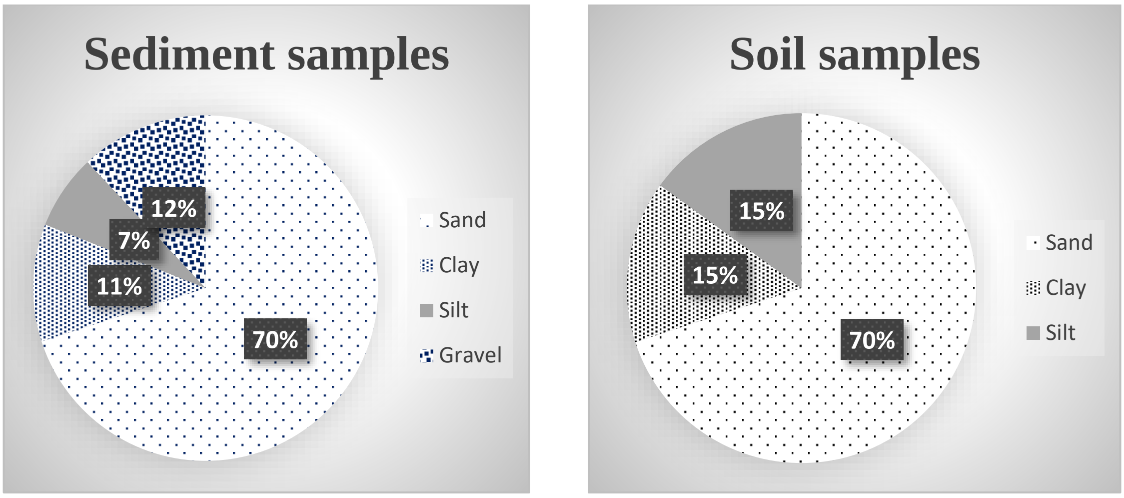


Figure 12. Classification of soil and sediment samples according to the distribution of particle size fractions

Multivariate hierarchy of clusters

The statistical analysis performed on the analyzed samples indicates a division of them into 2 main clusters and two sub-clusters (Figure 13).

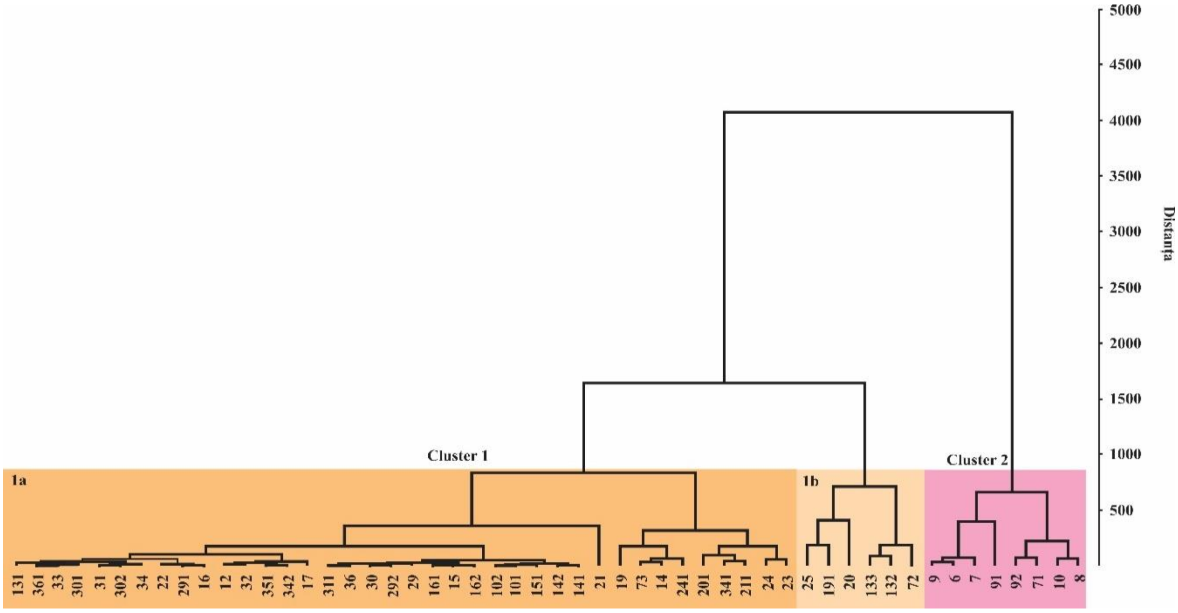


Figure 13. Cluster analysis for soil and sediment samples

Cluster 1 comprises 44 samples divided into two sub-clusters.

Sub-cluster 1a comprises a number of 38 samples (18 sediment samples and 20 soil samples) grouped according to the amount of Zn. The values of this element are between 42.27 mg/kg and 480.40 mg/kg. Cu, the second metal in terms of abundance, stands out, its values being between 7.43 mg/kg and 334.69 mg/kg. The texture of the samples included in this sub-cluster is mainly represented by sands.

Subcluster 1b comprises a number of 6 samples (3 sediment samples and 3 soil samples) grouped according to the amounts of Zn and Cu. Values for Zn vary between 479.87 mg/kg and 874.63 mg/kg. The amount of sand in these samples varies between 41.37% and 81.56%, the less coarse textures being characteristic of soil samples. Their texture is mainly represented by coarse granulometers.

Cluster 2 comprises a number of 8 samples (5 sediment samples and 3 soil samples) grouped according to the largest amount of Zn. The values of this element are between 1427.80 mg/kg and 1805.80 mg/kg. These samples are collected from the Lăpuș River, downstream of the mining perimeter in Băiuț. Their texture is mainly represented by sands.

Principal Component Analysis (PCA)

This analysis confirms the separation of samples into clusters and sub-clusters described above (Figure 38).

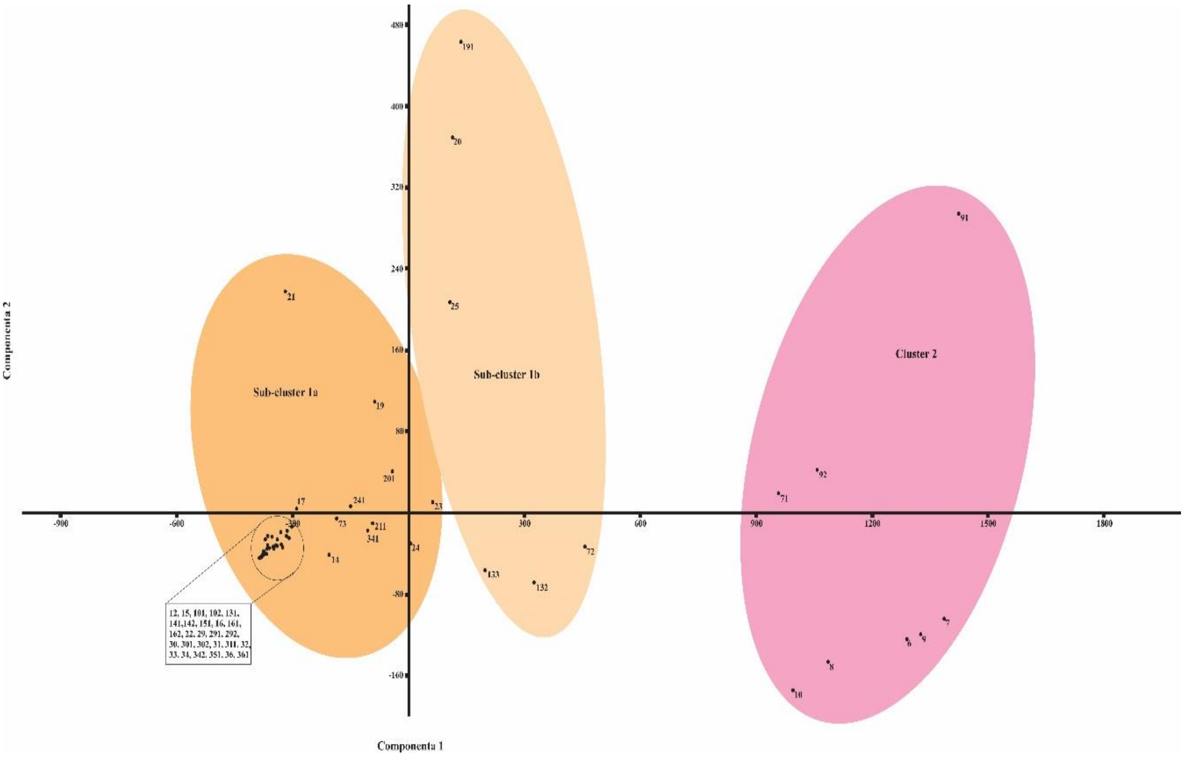


Figure 14. Principal Component Analysis (PCA

Component 1 generates 94.43% of the variance and groups only samples with positive values for all analyzed metals, noting Zn as the predominant element (> 0.8 correlation), along with Cu and Pb. Component 2 retains only 4.09% of the variance and groups the samples with positive values for Cu and Pb (> 0.6 correlation) and Ni, Cd and Cr (with a value below 0.2 correlation) these correlating negatively with the values Zn and Fe (correlation sub -0.2). Component 2 could indicate that although Zn is found in large quantities in the analyzed samples, it is possible that this element comes not only from anthropogenic activities but, to a relatively small extent, also from geogenic sources.

Folk and Ward parameters

Knowing that the distribution of different particle size classes numerically describes the transport and sedimentation process, their variation was studied along the middle and upper river basin of the Lăpuș River, from springs to the entrance to the protected gorge area. Having data on the distribution of particle size fractions, through the specific parameters of its distribution it can be appreciated how the clastic material was transported and deposited.A natural sediment is a heterogeneous dispersed system, comprising granules of micron size up to gravel elements of several cm. Four parameters describe, with sufficient accuracy, such a system: the average particle size $\mathbf{M_z}$, the particle size dispersion $\boldsymbol{\sigma}$, the asymmetry of the distribution $\mathbf{S_k}$ and the excess, $\mathbf{K_G}$ (Folk and Ward, 1957).

The relationship between the specific parameters of the distribution can be a good indicator in the interpretation of different environmental aspects related to the processes of transport and storage of sediments. The textural parameters of sediments are often sensitive receptors of the fluvial environment. (Folk and Ward, 1957; Friedman, 1961, 1967; Moiola and Weiser, 1968; Passega, 1957; Visher, 1969).

Since the variation of the presented parameters brings information on the formation of these sediments, it is recommended that these parameters be grouped two by two in four binary diagrams: M_z/σ, M_z/S_k, S_k/σ and S_k/K_G (Friedman, 1961). This method of analysis of particle size data emphasizes that a combination of pairs of these parameters has genetic consequences and indicates the peculiarities of sedimentation (Doroțan et al., 2020).

For the sedimentological study of the Lăpuş Basin, we examined, by distributing these parameters, the differences in the transport and sedimentation of mineral particles along the course of the river and its tributaries starting from the mobile sediment in the riverbed.

Along the course, the Lăpuş and its tributaries cross three distinct areas: the mountain area, the hill area and the alluvial plain itself.

The mountainous area is characterized by a high flow slope, by turbulent flow, and by the active influence of the valley slopes, generally narrow, in the form of a significant lateral contribution. It should be noted that the whole area comes from the solid granules containing heavy, toxic metals.

The hilly area is characterized by moderate runoff slopes, in wide valleys where the stream is flanked by meadows and terraces of varying sizes, but with low lateral input. The intake of granules containing toxic heavy metals is also low, reducing to the remobilization of those from older sediments.

Finally, the flow slope in the alluvial plain is low or almost zero (in the case of Dobric), the insignificant lateral input and the input of particles carrying toxic heavy metals depending only on high floods.

Consequently, a formation area can be distinguished, another transport area and the final one, the deposition area (Figure 15).

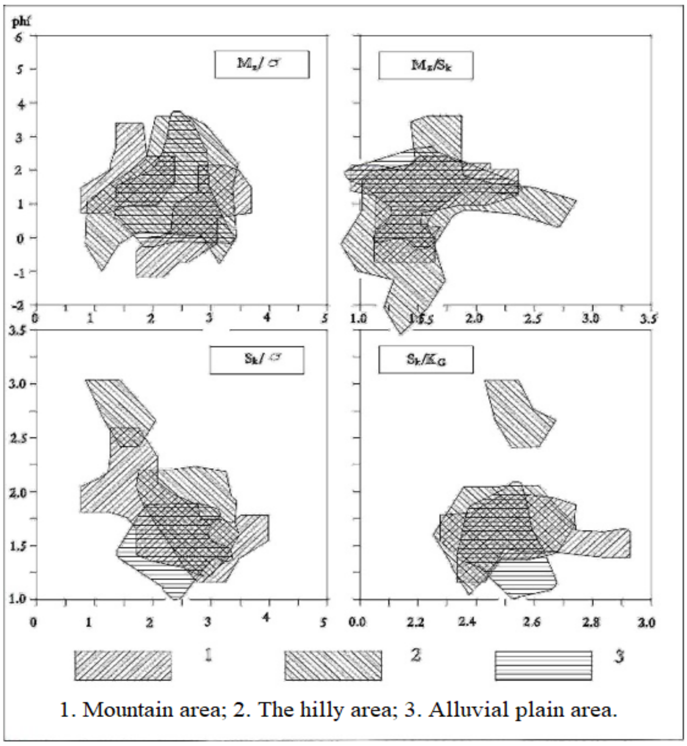


Figure 15. Distribution of granulometric parameters for the sediments of the Lăpuş river basin

From the figure above it is observed that the pairs of parameters occupy fields of different shapes and extensions for the three morphological units.

Student test

Following the separation of sediments from the mountain area, the hilly area and the alluvial plain, the question arises, whether this separation also occurs in the distribution of heavy and toxic metals. For this purpose, we performed the Student test for the elements Cu, Ni, Zn, Cd, Pb, Cr, Fe (Dorotan et al., 2020).

In case of normal or lognormal distribution, the Student`s t-test verifies, that in set M and N, the X {x, y} variable (ie the concentrations of the respective element) belongs to the same set, or forms two significantly different sets. For this, the following relationship will be applied:

$$t = \frac{x - y}{\sqrt{(n-1)s_x + (m-1)s_y}} \sqrt{\frac{nm(n+m-2)}{n+m}}$$

Where:

m- number of samples from M set

n- number of samples from N set

x- mean value of the concentration in set M

y- mean value of the concentration in set N

s_x- dispersion in set M

s_y- dispersion in set N

If the result is that $t<t_{adm}$ (i.e. the value established for the number of pairs and the desired significance level), the hypothesis H=0 is verified, there are not significant differences between these groups; in the opposite case, the groups differ from each other. In this study, the Student`s t-test was applied for Cu, Ni, Zn, Cd, Pb, Cr and Fe, at 0.05 significance level.

Table 11. Student test result for morphological units of the Lăpuș river basin.

Morphological zone		t value for heavy metals							Admisible value
		Cu	Ni	Zn	Cd	Pb	Cr	Fe	
Mountain	Hill	24.591	**1.073**	209.943	4.458	15.190	4.252	18.736	2.412
Mounain	Basin	19.301	7.734	114.856	**0.395**	8.501	9.374	22.369	2.861
Hill	Basin	**2.129**	5.758	36.506	**2.838**	3.831	5.209	6.702	2.861

From Table 11 it can be seen that for the seven elements analyzed, only cadmium - at the level of concentrations close to the detection level - satisfies the hypothesis H = 0 in the mountain-basin-hill-basin relationship, as well as for the copper contained in the hill sediments and basin, respectively nickel, between the mountain and the hill. Otherwise, the hypothesis H = 0 is not verified, the difference between the set of contents is significant. Therefore, the three morphological units differ not only in terms of sedimentology, but also in the transport and storage of heavy toxic elements.

VI. Environment quality assessment by using specific quality indices

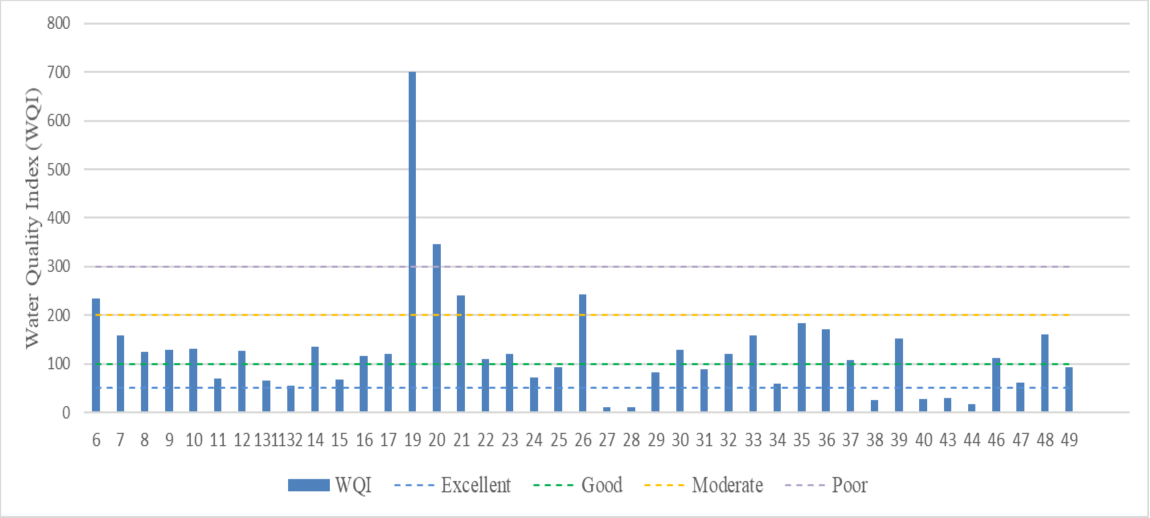
Evaluation of water quality by using specific quality indices

Different water quality indices that used to assess water quality of the Lăpuș river basin are presented in Table 12.

Table 12. Water quality indices

Index name	Formula	Pollution level
Water Quality Index (**WQI**)*	$WQI = \sum SI_i$	WQI<50→Excellent 50<WQI<100→Good 100<WQI<200→Moderate 200<WQI<300→Poor WQI>300→Highly polluted
Metal Index (**MI**)**	$\boldsymbol{MI} = \sum_{\boldsymbol{i=1}}^{\boldsymbol{n}} \frac{\boldsymbol{c_i}}{(\boldsymbol{MAC})\mathrm{i}}$	MI>1→Polluted water
Heavy Metals Pollution Index (**HPI**)***	$\boldsymbol{MI} = \sum_{\boldsymbol{i=1}}^{\boldsymbol{n}} \frac{\boldsymbol{c_i}}{(\boldsymbol{MAC})\mathrm{i}}$	HPI>100→ Polluted water
(* Shweta et al., 2013; ** Bakan et al., 2010; *** Mohan et al., 1996)		

The *Water Quality Index* ***(WQI)*** values for water samples ranged from 10.30 to 2295.54 (Figure 16). According to WQI classification, 13% of the studied samples have an excellent quality, 24% good quality, 42% moderate quality, 7% weak quality and 13% are very polluted.



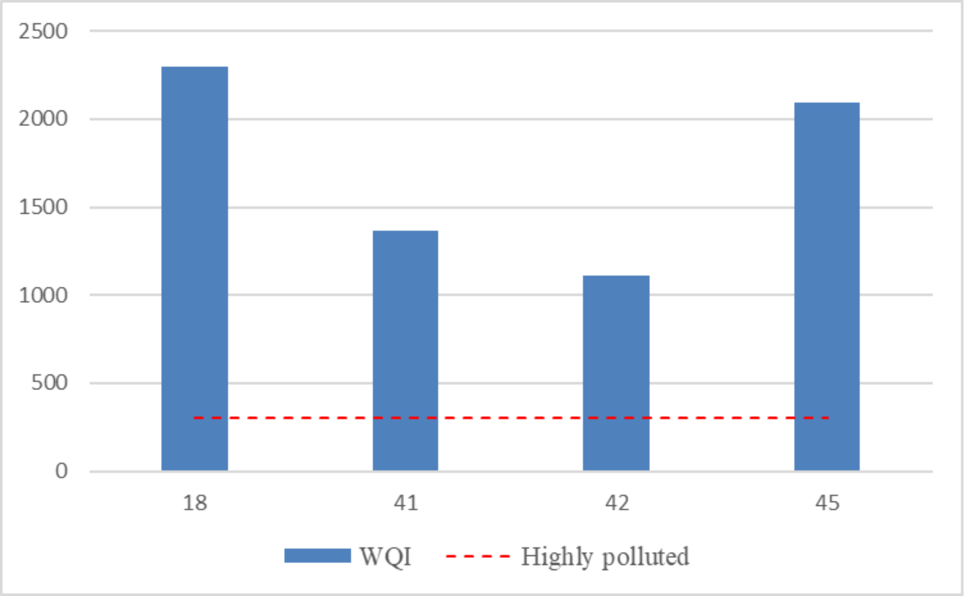


Figure 16. Variation of Water Quality Index (WQI) according to sampling point

All surface water samples had the value of *Metal Index **(MI)*** higher than the reference value (Figure 17). These ranged from 1.60 to 77.95. For mine waters the values were between 0.10 (sample 27) and 261 (sample 18).

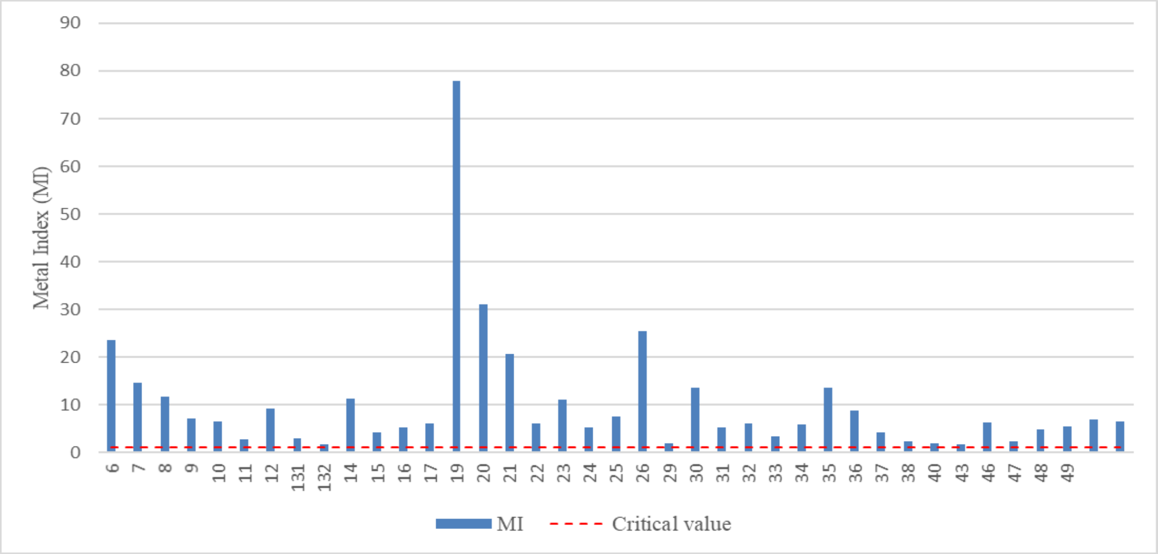


Figure 17. Variation of Metal Index (MI) for surface waters samples

The *Heavy Metal Pollution Index **(HPI)*** ranged from 2.42 to 7.112 in the case of mine water samples and from 4.52 to 1998 in the case of surface water samples (Figure 18). The highest values of the heavy metal pollution index were recorded in samples 18 and 45, the first being mine water (Gallery 8 - Poiana Botizii), and the second sample of water being taken from the base of the Bloaja tailings pond . 67.5% of surface water samples exceeded the critical value of 100 (Prasad and Kumari, 2008; Prasad and Mondal, 2008), which means that these waters, located near agricultural land can not be used for consumption.

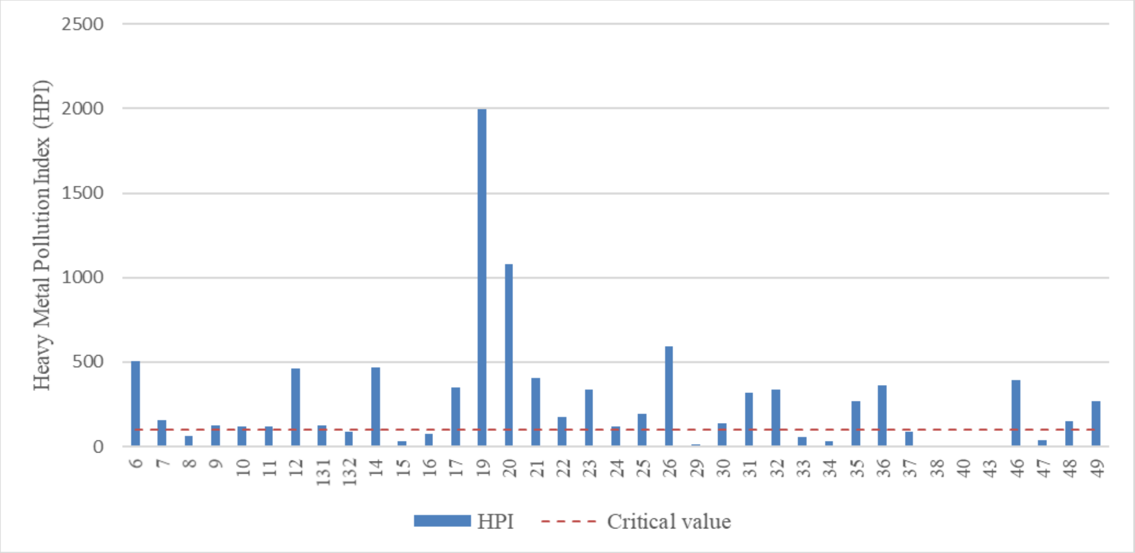


Figure 18. Variation of the Heavy Metal Pollution Index (HPI) in the surface water samples

Evaluation of soil and sediment quality by using specific quality indices

Table 13 presents different quality indices for soil and sediment quality assessment.

Table 13. Soil and sediment quality indices

Index name	**Formula**	**Pollution level**
Geoaccumulation Index (**$I_{geo\text{-}sol}$, $I_{geo\text{-}sed}$**)*	$I_{geo} = log_2(\frac{C_n}{1,5 * B_n})$	$I_{geo} \leq 0$→ uncontaminated $0 > I_{geo} < 1$→ uncontaminated to moderately contaminated $1 > I_{geo} < 2$→ moderately contaminated $2 > I_{geo} < 3$→ moderately to heavily contaminated $3 > I_{geo} < 4$→ heavily contaminated $4 > I_{geo} < 5$→ heavily to extremely contaminated $I_{geo} \geq 5$→ extremely contaminated
Pollution Load Index **(PLI)****	$PLI = \sqrt[N]{c_{f1} + c_{f2} + c_{f3} + c_{f4} + \cdots c_{fn}}$	0→Ideal <1→Uncontaminated >1→Progressive contamination
Sediment Pollution Index **(SPI)*****	$SPI = \sum(EF_m \times W_m)/\sum W_m$	0-2→Uncontaminated 2-5→Slightly contamination 5-10→Moderately contamination

		10-20→Heavily contamination >20→Extremely contamination
(*Müller, 1969; **Tomlinson et al., 1980; *** Singh et al., 2002)		

Following the *Geoaccumulation Index* ***($I_{geo-soil}$)*** calculation, the degree of pollution of heavy metals decreases in the following order: Cd> Zn> Pb> Ni> Cu (Table 14). According to Müller's (1969) pollution scale, there is no Cr pollution in the studied area.

The $I_{geo-soil}$ values ranged from -1.30 (P292) to 4.05 (P191) for I_{geo}Pb, 1.09 (P311) and 5.15 (P91) for I_{geo}Cd, -1.28 (P292) and 4, 08 (P91) for I_{geo}Zn, -0.63 (P292) and 1.48 (P341) for I_{geo}Ni and -2.18 (P292) and 3.27 (P91) for I_{geo}Cu.

Table 14. Geoaccumulation index ($I_{geo-soil}$) for soil samples

Value	Heavy metal				
	Cd	Zn	Pb	Ni	Cu
Minimum	1.09	-1.28	-1.30	-0.63	-2.18
Maximum	5.15	4.08	4.05	1.48	3.27
Average	3.11	0.65	0.60	0.17	-0.21

Following the *Geoaccumulation Index* ***($I_{geo-sed}$)*** calculation, the degree of pollution of heavy metals decreases in the following order: Cd> Zn> Pb> Cu. According to Müller's (1969) pollution scale, there is no Ni and Cr pollution in the studied area (Table 15).

The $I_{geo-sed}$ values ranged from -1.28 (P15) to 3.60 (P25) for I_{geo}Pb, 0.42 (P30) and 3.03 (P34) for I_{geo}Cd, -1.75 (P30) and 3, 66 (P7) for I_{geo}Zn, -3.18 (P30) and 3.01 (P20) for I_{geo}Cu.

Table 15. Geoaccumulation index ($I_{geo-sed}$) for sediment samples

Value	Heavy metal			
	Cd	Zn	Pb	Cu
Minimum	0.42	-1.75	-1.28	-3.18
Maximum	3.03	3.66	3.60	3.01
Average	1.90	0.68	0.60	-0.79

Pollution load index ***(PLI)*** values for soil samples (Figure 19) ranged from 0.61 (P292) to 8.44 (P91), 85% of the soil samples exceeded the reference value set as 1. The highest values were recorded for P91, P92 and P191. Sample 191 being taken from Valea Poienii (Poiana Botizii), and samples P91, P92 from the terrace of the river Lăpuş.

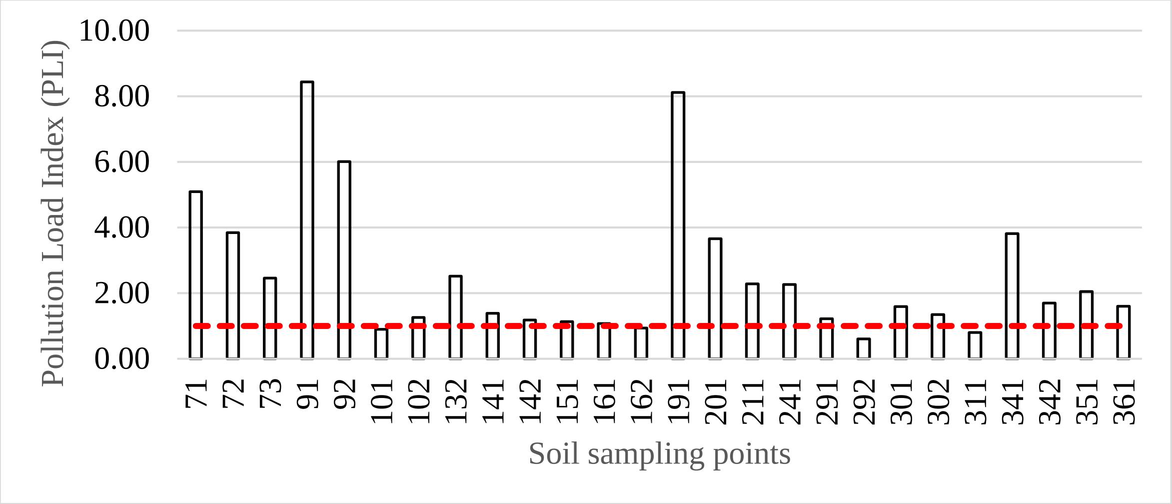


Figure 19. Pollution Load Index (PLI) values for soil samples

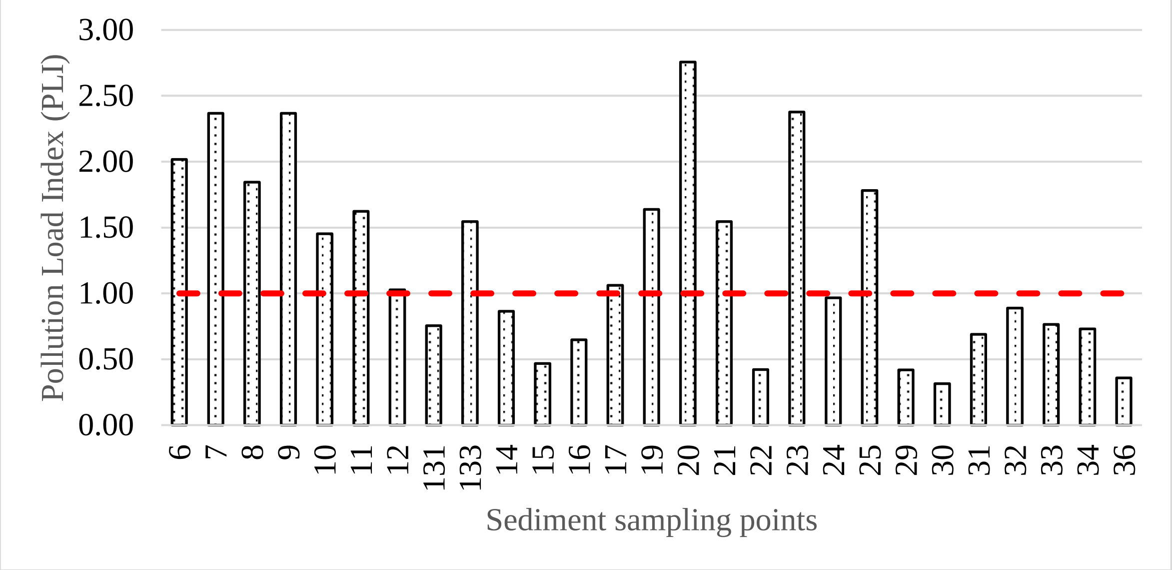


Figure 20. Pollution Load Index (PLI) values for sediment samples

In the case of sediment samples, the values of **PLI** (Figure 20), ranged between 0.31 (P23) and 2.76 (P20), 52% of the sediment samples exceeding the reference value set as 1. The highest value is related to a sediment sample taken from the Poienii Valley, which passes through the village of Poiana Botizii.

Regarding the *Sediment Pollution Index **(SPI)***, the values ranged between 0.91 and 9.20 (Figure 21), 33% of the sediment sampling points were uncontaminated, 41% were slightly contaminated and 26% were moderately contaminated. Most of the moderately contaminated sediments were taken from the main course of the Lăpuș River, signaling the existence of mining associated pollution.

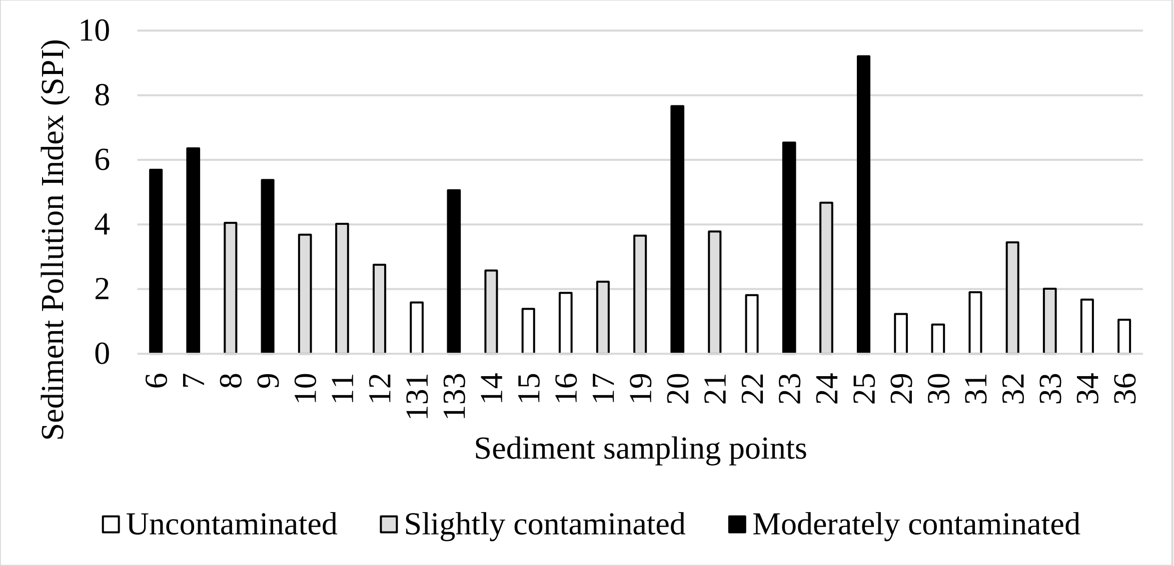


Figure 21. Sediment Pollution Index (SPI) values

VII. Conclusions

The middle and upper river basin of the Lăpuș River remains an area with high risk for the environment and population due to historical contamination from the former mining operation in Băiuț, this pollution having an impact on the Cheile Lăpușului Natural Reserve.

Accidental spills, such as those in March 2018 caused by melting snow, load the Lăpuș River with heavy metals, which have a direct effect on the fish fauna and the entire ecosystem.

The *general objective* of the thesis was achieved through the theoretical and experimental research activity and, by achieving the *specific objectives* mentioned in the introductory part of the thesis.

For each of the specific objectives the following can be concluded:

- Physico-chemical analyzes for surface water samples resulted in a ***pH*** between 5.43 and 7.80, indicating an acidic to basic character. The pH of the mine water samples had values between 2.84 and 8.05, causing the water to be very acidic towards the base.
- The ***pH*** values of the soil samples varied between 5.16 and 7.84, which determines the reaction of the soil as moderately acidic to slightly alkaline. The pH values of the sediment samples were between 6.57 and 7.91, therefore most of the samples can be classified as weakly alkaline.

- Following the determination of the concentration of ***dissolved ions***, the order of the concentration of the majority ions present in the surface water samples was: SO_4^{2-}> Ca^{2+}> Na^+> Cl^-> Mg^{2+}> NO^{3-}, and in the case of mine water samples it was: SO_4^{2-} > Ca^{2+}> Mg^{2+}> Na^+> K^+> Cl^-> NO^{3-}> F^-> Li^+. Sulfate ion had the highest values in both surface water and mining water, 67% of surface water samples were in quality class I, 30% in quality class II and 3% in quality class III. Regarding mine waters, 37.5% exceeded the maximum allowed concentration (H.G. 352/2005).
- Of the seven ***heavy metals*** studied, five were identified in the surface water samples, the order of their concentration being: Fe> Zn> Cu> Pb> Cr. The order of the concentration of heavy metals in the case of mine waters was: Zn> Fe> Cu> Ni> Cd> Cr> Pb. The order of the concentration of heavy metals in the soil samples was: Fe> Zn> Pb> Cu> Ni> Cr> Cd. The order of the concentration of heavy metals in the sediment samples was as follows: Fe> Zn> Cu> Pb> Ni> Cr> Cd.
- Following the ***granulometric analysi***s, the texture of the sediment samples is represented, mainly by sands, 70% of the samples having as predominant fraction sand, 12% gravel, 11% clay and 7% silt. The texture of the soil samples is mainly represented by sands, 70% of the samples have as predominant fraction sand, 15% silt and 15% clay.
- The ***statistical analysis*** performed on the analyzed samples indicates a division into 2 main clusters and two sub-clusters, grouped according to the largest amount of Zn.
- The analysis of the main components ***(PCA)*** confirms the separation of the samples into clusters and sub-clusters. Component 1 generates 94.43% of the variance and groups only samples with positive values for all analyzed metals, Zn being noted as the predominant element along with Cu and Pb. Component 2 retains only 4.09% of the variance and groups the samples with positive values for Cu and Pb, Ni, Cd. Component 2 could indicate that although Zn is found in high quantities in the analyzed samples, it is possible that this element comes not only from anthropogenic activities but, to a relatively small extent, also from geogenic sources.
- Through the ***binary combinations of the parameters specific to the particle size distribution***: M_z/σ, M_z/S_k, S_k/σ and S_k/K_G (Friedman, 1961), one can distinguish a formation area (mountain area), a transport area (hilly area) and the final one, for sediment deposition (alluvial plain). The combination of pairs of these parameters has genetic consequences and indicates the peculiarities of sedimentation.

- The separation identified from the mountain area, the hill area and the alluvial plain, also occurs in the distribution of heavy and toxic metals. This is confirmed by applying the ***Student's test*** for the elements Cu, Ni, Zn, Cd, Pb, Cr, Fe.
- Following the calculation of the ***Water Quality Index (WQI)*** for surface waters and mine waters, valuesranged between 10.30 and 2295.54, 13% of the samples studied are of excellent quality, 24% are of good quality, 42% have a moderate quality, 7% have a poor quality and 13% are highly polluted.
- The ***Metal Index (MI)*** had values between 1.60 and 77.95 for surface waters and between 0.10 and 261 for mine waters.
- The ***Heavy Metal Pollution Index (HPI)*** varied between 2.42 and 7.112 in the case of mine water samples and between 4.52 and 1998 in the case of surface water samples. 67.5% of the surface water samples and 62.5% of the mine water samples exceeded the critical value (100).
- In terms of indices determined for the evaluation of water for irrigation use: ***Sodium absorption ratio (SAR), Sodium content (% Na), Percentage of soluble sodium (SSP), Salinity potential (PS), The Magnesium Ratio (MH), Magnesium Ratio (MR) and Kelley Index (KR)***, all the surface water samples studied are suitable for use for this purpose.
- Following the calculation of the ***Geoaccumulation Index*** for soil samples ***$I_{geo\text{-}soil}$***, the degree of pollution of heavy metals decreases in the following order: Cd> Zn> Pb> Ni> Cu, and in the case of ***$I_{geo\text{-}sed}$*** the degree of pollution of heavy metals decreases in the following order: Cd> Zn> Pb> Cu. The highest values were recorded for cadmium in both soil samples and sediment samples.
- The values of the ***Pollution Load Index (PLI)*** for the soil samples were between 0.61 and 8.44, 85% of the soil samples exceeding the reference value set as 1. In the case of sediment samples the PLI values were between 0.31 and 2.76, 52% of the sediment samples exceeding the reference value. - The sediment pollution index (SPI) varied between 0.91 and 9.20, 33% of the sediment collection points are uncontaminated, 41% are slightly contaminated and 26% are moderately contaminated.

The originality of this study is represented by the application and use of quality indices for water, soil and sediment in order to assess the quality of the environment in the studied area.

Although numerous studies have been performed on the concentration of heavy metals (Bird et al. 2003; Macklin et al. 2003; Bird et al. 2005; Horvath et al. 2009) in environmental factors, the index model has been applied for the first time in this area, in the present doctoral thesis. Furthermore, the study on the particle size composition and its connection with the concentration of heavy metals is also applied for the first time in this area.

Through the research activity related to this doctoral thesis, new perspectives and opportunities have been opened, through which the decision-makers as well as the local community can be aware of the need to take environmental protection measures regarding the pollution generated by acid waters in Băiuț, which poses a threat to the entire Lăpuș River ecosystem. This thesis can be the basis for future research, providing the opportunity to identify scientific data and use them in other specialized studies.

Further development perspectives:

- Extension of the study area on the entire river basin of the Lăpuș River;
- Research on the transfer of pollutants from soil to plants by determining the concentration of heavy metals in vegetation;
- Research on groundwater contamination due to acid mining drainage;
- Research on the health problems of the residents in the vicinity of E.M. Băiuț;
- Air pollution due to wind erosion caused by dams in the vicinity of the Bloaja tailings pond, as well as a study on the erosion and leakage phenomena of this pond;
- Given the drastic reduction of fish fauna in the last 5-10 years, it would be necessary to investigate the bioaccumulation of heavy metals in aquatic organisms.

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***Hotărâre nr. 352 din 21 aprilie 2005 privind modificarea şi completarea Hotărârii Guvernului nr.188/2002 pentru aprobarea unor norme privind condiţiile de descărcare în mediul acvatic a apelor uzate