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ACCUMULATION OF HEAVY METALS IN SOILS AND ALLUVIAL DEPOSITS OF LĂPUŞ RIVER, MARAMUREŞ COUNTY, ROMANIA

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Abstract: The abandoned mining sites related to uncontrolled mine waste and acid mine drainage are one of the most serious environmental problems of Romania. The mining activities in Romania started to decline since the 90's when economically has become unprofitable, but the consequences on the ecosystem begin to emerge: drastic decline of fish fauna, drying of the riparian vegetation of floodplains. The Baia Mare mining region offers numerous, and well studied examples for this problems. The Upper Lăpuş Valley was selected by us because of the presence of a typical terrace system, and the lack of other (no mining) industrial pollution sources. Therefore, sampling the successive levels, beginning from the actual riverbed, until the Pleistocene terrace, the historical and industrial heavy metal inflow can be separated to the natural (geological) background. The Zn, Cu, Pb and Cd concentrations in soil samples of the upper level of the floodplain are higher, that the background, reaching in some samples the attention level. The values for heavy metals are between 4.90 – 2015 ppm for Cu, 0.50 – 50.90 ppm for Cd, 5.00 – 1050 ppm for Pb and between 21.00 – 5050ppm for Zn. It is evident, that there are a *historical pollution*, tied to the pre-industrial mine works from Băiuţ area and to the activity of the Rojahida furnace plant. The pollution front advances downward both in alluvia and in soils of floodplain, menacing all of Lăpuş Valley, including the protected area of Lăpuş Gorge. Spreading the mineral particles in soil cover, the heavy, toxic metals will be accumulate in feedstuff, in crops and finally, in human foods.

Key words: heavy metals, mining waste, pollution, environment, stream sediment.

1. HEAVY METALS, MINING WASTE, POLLUTION

First of all, it is important to define some basic terms as Heavy (toxic) metals, Mining waste and Pollution, because these ones are used in some papers, having different and in more case, inaccurate, or confuse sense (Appentroth, 2010).

1.1. Heavy metals

In 1936, Bjerrum defined heavy metals as those metals with an elemental density above 7 g/cm^3. In time this value was decreased to 6, and later, to 5 or 4.5 g/cm^3, including some usual metals in rock forming minerals, as Fe and Mn. These elements are considerate as pollutant heavy metals, when they form toxic compounds, which cannot be decomposed by biological activity and remain in long time in soils and sediments (Adriano, 2001).

The heavy, toxic metal compounds cannot be nor generated, neither neutralized by biological processes (Fairbrother et al., 2007).

The dispersal, storage and remobilization of sediment-associated metals in the fluvial system can be directly related to sediment transport processes (Taylor & Kesterton, 2002; Walling et al., 2003), styles of river channel and floodplain sedimentation (Middelkoop, 2000) and flooding regime (Dennis et al., 2003).

Elements as Cu, Pb, Zn and Cd are the main, pollutant heavy metals issued from the base metal mining of Baia Mare region, and from Băiuţ plants, as well.

1.2. Mining waste

Taking out the mineral assemblage (ore or rocks) stable in the depth, in surface condition, by the change of P, T, pH and redox potential a new chemical mineralogical equilibrium will be realized. Together with the physical-mechanical transformation, new minerals as clays, oxides, hydroxides, soluble salts etc. will be formed, with or without release of heavy metals in environment. Thus, mining activity generates important volumes of rocks with changed properties, both as utile (ore) and waste (sterile) material. The ore concentrate contains quartz, calcite, rock fragments etc., and in sterile, a few percent of metallic minerals, (mainly of pyrite), together with their heavy metal contents can be found.

The mining waste consists in subaerial deposits of coarse grained fragments (heaps, tailings) and fine grained accumulations (dumps, ponds). In unprotected, abandoned sites, the natural background is invaded by solid mineral particles and more or less concentrated solution of heavy, toxic metals from these accumulations (Salomons, 1995; Passariello et al., 2002; Baciu & Costin, 2008).

1.3. Pollution

All of heavy metals are part of the natural composition of ores, rocks and soils, from where they are mobilized in the soluble components of the natural water flows as well. They become pollutant ones, when (i) they are coming from a human activity and (ii) the concentration of them show significantly higher values, than the natural background. Thus, the term pollution appears as unnecessary, when the anthropic source is missing, or the natural background is unknown (Greger, 2004)

2. GEOLOGICAL FRAMEWORK OF UPPER LĂPUŞ VALLEY

2.1. Regional and local geology

The Lăpuş valley springs from the Eastern segment of Oaş-Gutâi-Ţibles Neogene Igneous Mountain Range, i.e. from the Vǎratec Mts. Here one of the most complicate geological built-up of Eastern Carpathians was deciphered: lying on Hercynian metamorphic basement, a Jurassic-Neocomian Piennine klippe and Upper Cretaceous and Paleogene clastic deposits belonging to Oligocene Autochtone and three nape units are developed, under the Badenian, Sarmatian and Pannonian post tectonic cover (Bombiţă, 1972). Around the 9–10 My K-Ar aged intermediate igneous rocks as lava flows and intrusive bodies contact metamorphic rims, hydrothermal alteration fields and vein-like or breccious hydrothermal (Borcoş et al., 1972) base metal and Au-Ag bearing ore deposits were formed.

The object of mining activity in Băiuţ area was the vein-like and massive base metal and Au-Ag ore (Mariaş, 2005), located in Paleogene and Sarmatian clastic rocks and in Neogene igneous stocks, plugs or subvolcanic bodies. Three main structures were exploited: Brainer (with Providenţa Divină and Robu lodes), Vǎratec (with Alexandru, Ioan and Botiza I-IV lodes) and Poiana Botizii (with Cizma and Coasta Ursului lodes).

The main ore minerals are pyrite, pyrrhotite, chalcopyrite (Cizma), sphalerite, wűrtzite, arsenopyrite, galenite, tetrahedrite, bournonite (Alexandru-Vǎratec), antimonite (Robu), native gold (Alexandru), different sulpho-salts in upper part of the lodes, hydrothermal and secondary hematite, goethite, marcasite, cerusite and malachite (Manilici et al., 1972; Costin, 2002). The non metallic minerals are represented by quartz, chalcedony, calcite, siderite, barytine (Robu), alunite (Ioan Nou), clay minerals as kaolinite, montmorillonite, gypsum and pyrophyllite (both in Roşia veins).

2.2. Morphology

After Posea (1962) the Quaternary evolution of the Upper Lăpuş Valley begun during the Levantin/Pleistocene boundary with Pedi planation of Munceilor surface and continue with formation of seven terrace levels. Four of these ones (including the upper part of the floodplain) were identified between Strâmbu Băiuţ village and the confluence of Lăpuş with Ruoaia rivulet. The age of these terraces, supposed by morphological correlation are Early Holocene (the upper level of the actual floodplain) and Late Pleistocene (leftward the Ruoaia Platform and in right side of the valley the Podirei terrace).

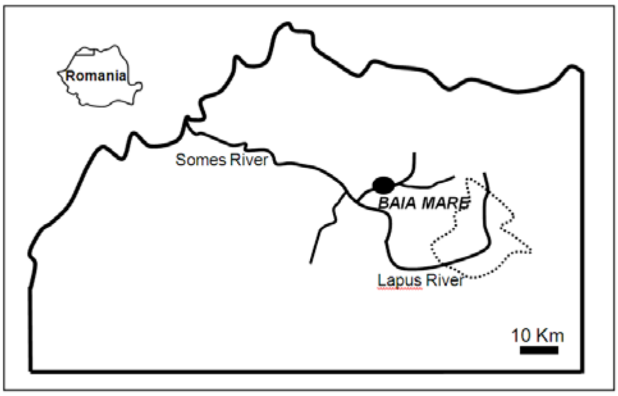

Figure 1. Lăpuş River basin (after Costin & Baciu, 2010 - with modifications).

The floodplain of Lăpuş River (Fig. 1) begins from the confluence between Băiuţ and Strâmbu rivulets (Strâmbu Băiuţ village) forming a 50–450 m large, gently undulated surface, mainly on the left side of the river. Down to confluence with Poiana stream, two sub-levels are recognized: the upper sub-level, at 2–4 m and the lower one, at 0.5-1.5 m up to the riverbed. Note, that during the floods, the lower sub-level is overflow, while the upper sub-level is coming under waves only in case of catastrophic rainfalls (e.g. in May, 1970).

3. THE MINING ACTIVITY IN BĂIUŢ AREA

3.1. Mining works and processing of the ore

Apart of small quarries opened during last years of the mining activity, the vein-like base metal ore bodies were opened by transversal galleries (from surfaces or from mine pits). They were followed by directional galleries, divided in panels by ascending works and the ore was extracted in roof battings, using explosive charges. The bulk ore was transported to the flotation processing plant in which, the Pb-Cu, the Zn and the (gold bearing) pyrite concentrate were retained, and the sterile slurry was released in four ponds. Together with the slightly alkaline flotation slurry, the acid mine water from Brainer mine was reversed in these ponds, neutralizing them.

Closing the mines and the flotation plant, in Băiuţ area (in despite of the substantial expenses of the "closing works"), there are large extended mine waste deposits and the acid mine water flow continuously in Tocila and Băiuţ streams. In the area was estimated an amount of nearly 1.300.000 m^3 coarse grained material and 900.000 m^3 flotation sterile tailings. While the coarse material of some heaps was transported both from Băiuţ (because their small gold content) and from Cizma galleries (as road fillings), the main problems issue from the uncovered dumps with deep erosion ditches both in Leorda and in Bloaja valley. Note, that on the platform of the lower Bloaja dump, a few thousand tones of mixed (Pb, Zn) ore concentrate was abandoned.

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

4. FIELD WORKS AND ANALYTICS

Knowing the trans-national character of the mining pollution in Carpathian Region a research project founded by the European Union and Norway was implemented (Horvath et al., 2009). Our paper presents a part of the results of this project focused for Băiuţ area, in which collaborated Romanian and Hungarian scientists and field workers of Mining Research Institute, Baia Mare; Babeş-Bolyai University, Cluj-Napoca and Geological Institute of Hungary, Budapest.

Seeing the problems approached by (Chira et al., 2014) we follow the next research in stream and terrace sediment in our study.

4.1. Field works

The first step of our environmental study was to collect samples both from Lăpuş Valley and from geological background of them.

In Lăpuş Valley, samples were taken in five cross sections (Fig. 2, Fig. 3), from right riverside, from riverbed, from stream sediment, from left riverside and from terrace deposit of the last two sections.

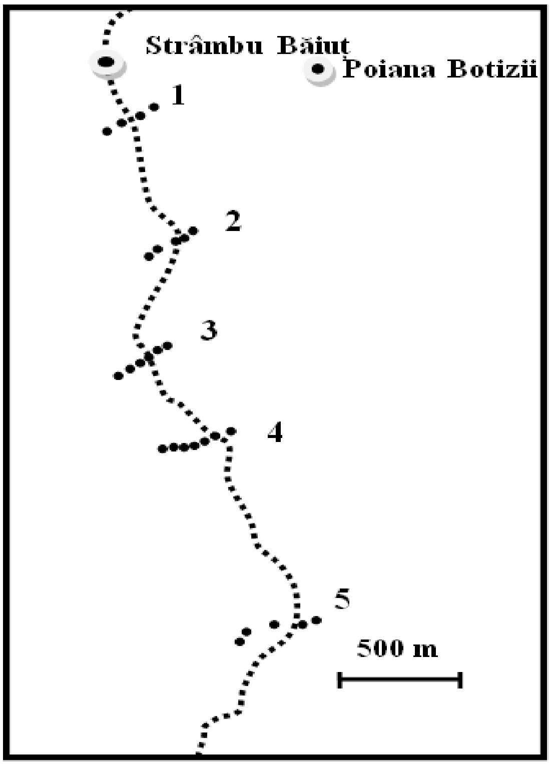

Figure 2. Sample location in Lăpuş Valley.

Apart of stream and riverbed sediments, the soil samples were taken below plough level in shallow (0.6-1.5 m) boreholes. These samples were closed in plastic tubes and were conserved at 4°C until to be analyzed (STAS 7184/1–84).

In order to establish the natural background level of samples, we took in consideration the published values for flood plain sediments (Salminen, 2005), in comparison with the local background. Regarding the local values of the litho-geochemical background, we sampled eleven of the main extended formations from Upper Lăpuş hydrographic basin (Doroţan et al., 2010) including the values of Lăpuş Formation (Kalmár & Macovei, 2011), because this last rocks form the riverbed of Lăpuş beginning from Gura Poienii til the mouth of Ruoaia stream. The rock samples were taken from outcrops in small quarries or from road excavations, under the weathered level, far out of hydrothermal alteration areas. The marly-sandy levels of Lăpuş Formation were sampled in large outcrops Râpa Malului – Rogoz village. The background values were obtained balancing the contents with outcropping area of the sampled rocks.

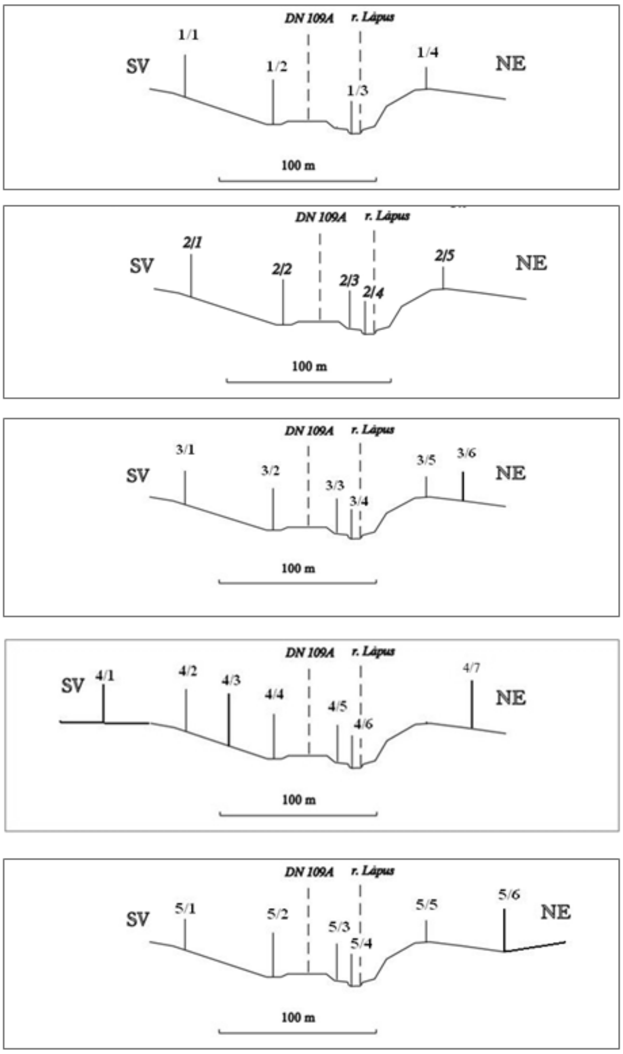

Figure 3. Distribution of the sampling points across the valley.

4.2. Analyses

The stream sediment, the alluvia, the borehole and the rock samples were dried, milled at <0.063 mm and digested with *aqua regalis*. Using JY Ultima2 ICP-OES spectrometer in chemical laboratory of thethe Hungarian Geological Institute, 23 main and trace elements, including the heavy, toxic metals

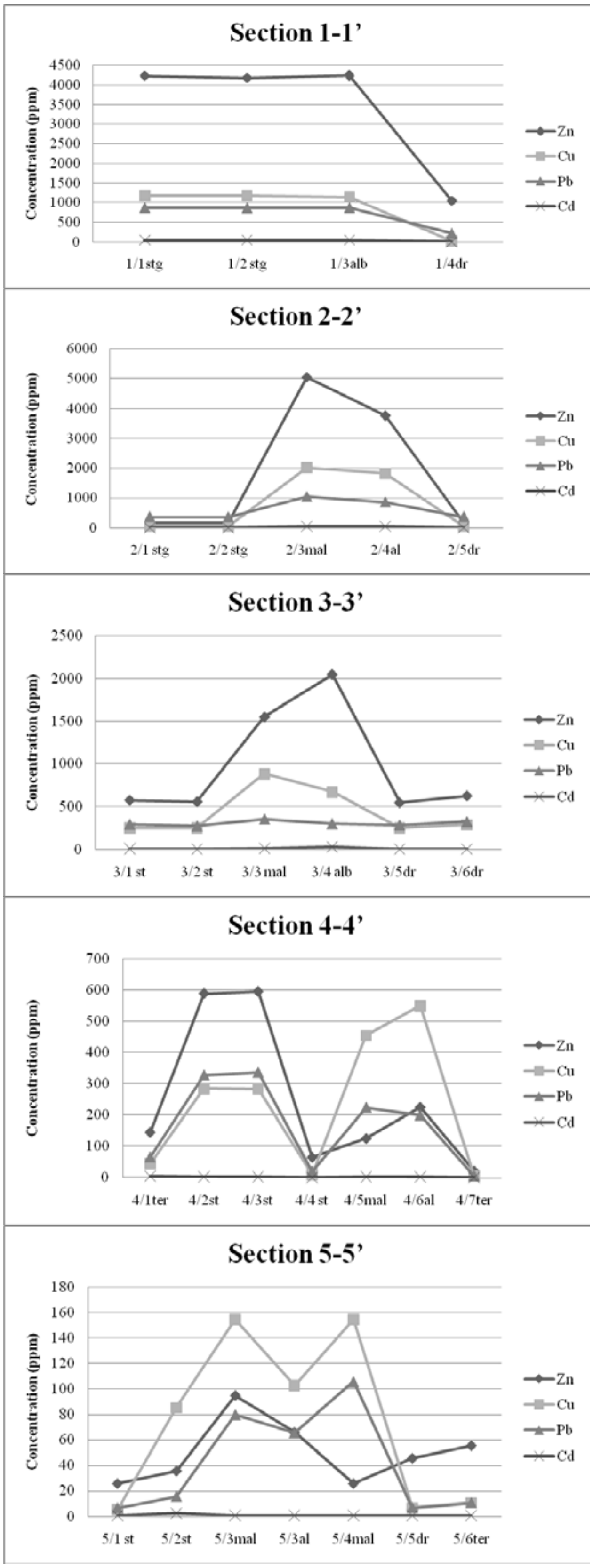

Figure 4. Distribution of heavy metals across the valley section

were analyzed. We analyzed under binocular microscope and in polished pellets the composition of sand grains in 0.1–0.2 mm fraction of a few stream and alluvia samples, in which electron microscope photos were executed, too (Laboratory of the Physics of Solid Materials, University of Debrecen, Hungary).

5. RESULTS

From the 23 main and trace element, we selected four heavy, toxic metals: Cu, Pb, Zn and Cd. Based on the analytical data (Table. 1), the variation of the contents across the Lăpuş Valley (Fig. 4) and along the valley line (Fig. 5) can be followed. Comparing the analytical data for the morphological levels of Lăpuş Valley, we attempt to distinguish the industrial, historical and geological charge of sediments and soils with heavy, toxic metals. Finally, knowing the background values, and the anomalous contents prescribed by Romanian environmental rules, the present state and the expected evolution of the analyzed sediments and soils will be presented.

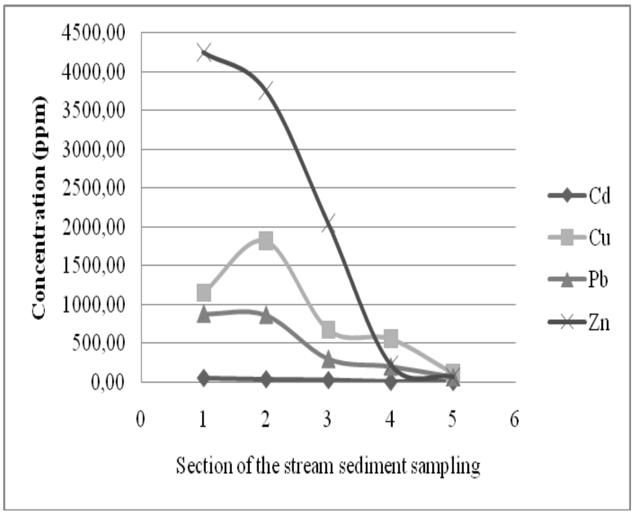

Figure 5. Distribution of Zn, Cu, Pb, Cd in stream sediment along LăpuşValley.

5.1. The distribution of heavy metals across the valley

In the first cross section (Fig. 4) in the alluvia, mainly the material from the dismembered concentrate deposit of Lower Bloaja dump, (situated leftward to the Lăpuş River) was found.

The ore concentrate, mixed with natural sand grains persists in left flood plain deposit, crosscut in sample 2/3 of the second section (Fig. 4), in which the metal contents are higher, than in the stream sediment. The samples 2/1 and 2/5, with low metal contents pinches an erosion shelf which marks the start of +5–8 m high Upper Pleistocene terrace level on both riverside.

Table 1. The heavy metals content in samples

Sample No.	Profil No.	Cu	Cd	Pb	Zn
	(ppm)				
14	1/4dr	27,5	50,60	220	1050
13	1/3al	1144,0	49,40	879	4251
12	1/2 stg	1180,0	50,90	870	4183
11	1/1stg	1175,0	0,50	879	4238
15	2/1 stg	38,2	0,50	375	163
16	2/2 stg	39,0	0,50	365	164
17	2/3mal	2015,0	0,50	1050	5050
18	2/4al	1820,0	45,00	865	3760
19	2/5dr	38,2	35,00	376	156
33	3/1 st	252,0	4,64	295	573
34	3/2 st	248,0	4,58	273	555
35	3/3 mal	885,0	12,00	355	1550
36	3/4 al	670,0	25,00	300	2050
37	3/5dr	250,0	4,56	285	544
38	3/6dr	288,0	2,37	325	624
44	4/1ter	45,0	5,00	65	145
45	4/2st	285,0	2,28	329	590
46	4/3st	284,0	2,24	338	596
47	4/4 st	10,7	0,50	19	64
48	4/5mal	455,0	2,50	225	125
49	4/5al	550,0	2,50	200	225
50	4/6ter	4,9	0,50	5	21
55	5/1 st	5,1	0,50	7	26
56	5/2st	85,5	2,25	16	36
55	5/3mal	155,0	0,50	66	95
53	5/3al	103,0	0,50	80	66
54	5/4mal	155,0	0,50	106	26
52	5/5dr	6,5	0,50	7	46
51	5/6ter	10,5	0,50	11	56

Sample location: ter - from the terrace; st - left bank of the river; mal - floodplain; al – stream sediment; dr – right bank of the river.

High contents in stream sediment, moderate ones in sample 3/3 from a strengths lower floodplain strip in left riverside, lower contents in sample 3/2 (left high floodplain) 3/1 and 3/5 were obtained. Increased contents of Zn, Cu, Pb appear in sample 3/6 of terrace level — this is the situation in the third cross section (Fig. 4), a bit down to the mouth of Ursului Valley.

The fourth section (Fig. 4) departs from the middle of the well developed plain of the Upper Pleistocene ("Ruoaia") terrace, with remarkable heavy metal contents. Coming downward, on the high floodplain, the samples 4/2 and 4/3 cut the filling of the former courtyard of the Rojahida furnace plant, which has processed, among others, the limonitic iron ore from the Roşia quarry — i.e. the oxidation zone of a large hydrothermal plug. The sample 4/4 reach the "fresh" high floodplain, while in the point 4/5, the (often overflowed) lower floodplain was sampled. After the high contents of the riverbed sediments, the contents fall down, reaching the geological amounts in sample 4/6 on the back of the right Pleistocene (Podirei) terrace.

The fifth cross section (Fig. 4) shows a close similarly situation: leftward higher metal contents in spreading fan of the former plant, on the lower level of the floodplain and small contents on the terraces of both riverside. The contents of the stream sediment are lower, that the contents of the floodplain soil.

5.2. The distribution of the heavy metals along Lăpuş Valley

By the dilution with siliciclastics from banks and affluent, or by self-erosion and leaching of the ore particles, downward of the river both the chemical and mineralogical analyzes show a decreasing amount of minerals and/or of metal contents in stream sediment (Fig. 5). Thus, the content in Zn decreases 65 times from first to fifth section (Table 2). Differences among the rate of decreasing may be explained with differences of the density of guest minerals or with inhomogeneous source material (i.e. of the Bloaja dump). In despite of decay of mineral particles, it is probable, that the relatively high heavy metal contents are persisting in red, iron hydroxide bearing mud sediment, which covers the riverbed till Târgu Lăpuş, on more than 35 km distance.

Table 2. The heavy metals content in stream sediments

Section No.	Profil No.	Cd	Cu	Pb	Zn
	(ppm)				
1	1/3al	49,40	1144,0	1050	4251
2	2/4al	45,00	1820,0	879	3760
3	3/4 al	25,00	670,0	300	2050
4	4/5al	2,50	550,0	200	225
5	5/3al	0,50	103,0	80	66

The floods charge the lower level of the floodplain with sediments in which the ore particles with heavy metal content are present. From the second to the fifth section, the heavy metal contents decreases for Zn, at 57 time; Cu, at 17 time; for Pb, at 11 time and for Cd, at 90 time (Table 2). The accentuated decay of Zn and Cd may be explained both by mechanical self-erosion of the sphalerite, and by biological consumption of these elements.

The high flood plain is "visited" by Lăpuş River only during rare catastrophic floods. In such a case among the enormous quantity of solid debit, the ore particles play insignificant role. Thus, the heavy metal contents in soil are relatively low, decreasing slowly downward.

If we consider, that the actual cutting ad deepening of the riverbed has produced beginning of industrial activity (i.e. the road construction using the gravels from the riverbed), in the historical past, the actual "high" floodplain has played the same role, like the actual "low" floodplain. Thus, the fall of Pb content from ~300 ppm to~200 ppm between section 3 and 4 marks the "front" of pre-industrial mining, no older, that 1000-1200 years.

Table 3. Local, general backgrounds and the reference levels of authorities (* after Doroţan et al., 2010; ** after Wedepohl, 1995; ***after Salminen, 2005)

Items	Zn, ppm	Cu, ppm	Pb, ppm	Cd, ppm
Stream sediment	2070	857	502	24.48
Lower floodplain	1750	778	428	15.00
Upper floodplain	227	85	186	1.82
Upper floodplain+furnace plant	253	146	222	1.82
Right Pleistocene terrace	227	85	186	2.66
Left Pleistocene terrace	409	144	187	1.49
Background values (* after Doroţan et al, 2010; ** after Wedepohl, 1995; ***after Salminen, 2005)				
Local background*	55	16	12	0.50
Mean stream sediments**	60	3	14	0.05
Mean floodplain sediments***	56	3	16	0.10
Reference data after Order No. 756/1997				
Attention level	300	100	50	3.00
Intervention level	600	200	100	5.00

Table 4. Frequency of exceedance of alert and intervention values compared to Romanian legislation

No	Monitorized Element	Frequency of exceedance %		Reference data – Order No. 756/1997, (mg/kg)	
		Attention	Intervention	Attention	Intervention
1	Pb	79%	69%	50	100
2	Zn	48%	31%	300	600
3	Cu	62%	52%	100	200
4	Cd	38%	28%	3	5

On the other hand, the "old" floodplain is overcharged with the waste of Rojahida furnace plant. In samples 4/2 and 4/3, 590–596 ppm Zn, 284–285 ppm Cu, 329–338 ppm Pb and 2.24–2.28 Cd appear in the soil, together with charcoal and slag fragments and fired rock debris. This is a clear example of the "historical" pollution.

Sampling the Upper Pleistocene terrace, deposited by former Lăpuş River and the affluent of them, more, that 15,000 years ago, surprisingly high contents of heavy metals were found: 458–544 ppm Zn, 250–382 ppm Cu, 285–376 ppm Pb and 4.5–5 ppm Cd under the actual plough level. Comparing with National Standards for Soil this Pleistocene values pass over the National Standard (Table. 4). It is possible, that here were sedimented fragments of the metal *rich heads* of the untouched ore bodies.

5.3. Local, general backgrounds and the reference levels of authorities

To have a global image of the pollution in the studied area we used the average values from table 1 taking into account the location of the samples in different morphological units. Thus, result the following categories: Stream sediment, Lower floodplain, Upper floodplain, Right Pleistocene terrace, Left Pleistocene terrace. In table 3, the values of the stream sediment and of the soil samples of different morphological units in comparison with the background values are presented.

6. DISCUSSION

Considering all of data, the pollution phenomenon appears as evident. Comparing the results with standardized values, the alert and intervention thresholds for sensitive soils under Order 756/1997 (Table 1, Table 4) it can be concluded that for Zn, Cu, Pb and Cd, 48%, 62%, 79%, 38% of samples show higher values, that the attention level and in 31%, 52%, 69% and 28% of samples, the intervention appears as justified. Sampling the whole section of Lăpuş Valley, different kind of "pollution" can be defined, now.

Thus, the most important (and most dangerous) pollution is the floating ore mineral particles, coming from the abandoned concentrate deposit on the back of Bloaja dump and spread both in alluvia, and — during the floods — in lower floodplain with intense agricultural activity. While the behavior of heavy metals in riverbed is tied to the peculiarities of the transport and deposition of solid phase (Wolfenden & Lewin, 1978; Bradley, 1984; Lewin & Macklin, 1987; Graf, 1990; Axtmann & Luoma, 1991), the spreading of them is dependent to the flood regimen (Connell & Miller, 1984; Graf et al., 1991; Marron, 1992; Lecce & Pavlowsky, 2001; Middelkoop, 2000; Taylor & Kesterton, 2002). The Lăpuş River, flowing from Strâmbu village 620 m ASL (Above Sea Level) to Târgu Lăpus town (330 m ASL) with speed stream segments, carries the sediments including the heavy metal bearing particles in pulsation regimen (Martin & Meybeck, 1979). Thus, the "front" of the wandering ore grains is situated now between the sections 3 and 4, but year by year it advances southward. The red mud, precipitated from the acid mine water, in present day is reaching the bridge of Târgu Lăpuş town.

The flood regimen of Lăpuş River is characterized by three or more yearly floods: in spring, in June and during the autumnal rainfalls. Together with the natural, mainly siliciclastic floating material, the ore particles are deposed in floodplain. Here, by agricultural activity is mixed in soil and the heavy, toxic metals will be immobilized for long time (Weber et al., 1991; Stevenson, 1994).

The Zn, Cu, Pb and Cd concentrations in soil samples of the upper level of the floodplain are higher, that the background, reaching in some samples the attention level. It is evident, that there are a *historical pollution*, tied to the pre-industrial mine works from Băiuţ area and to the activity of the Rojahida furnace plant.

Even if the anthropic factor is missing us face polluted zones. Here a natural, geochemical anomaly can be defined, which explains the high concentration in Pleistocene sediment in both sides of the valley.

7. CONCLUSIONS

In the Upper Lăpuş hydrographic basin, after thousand years, the base metal and Au-Ag mining activity was ceased, leaving behind unclosed gallery mouths, abandoned tailings, dumps and rests of ore concentrates. The acid mine water flows out continuously and the ore particles with high concentration in heavy, toxic metals are carried in rivulets and in main river, Lăpuş.

Knowing this alarming situation, in frame of an European project we studied the most menaced segment of this river, by systematic sampling of the whole cross section, analyzing the stream and soil samples and comparing them with the local and European background. Thus, we distinguish (i) the effects of the industrial pollution, produced mainly by uncovered flotation dumps with rests of ore concentrates, (ii) the prints of historical, pre-industrial pollution and (iii) the proves of the erosion of the ore bodies during the far past, which caused natural, geochemical anomalies on the sediments of Upper Pleistocene terraces.

The results of our analyses prove that the pollution front advances downward both in alluvia and in soils of floodplain, menacing all of Lăpuş valley, including the protected area of Lăpuş Defile. Spreading the mineral particles in soil cover, the heavy, toxic metals will be accumulate in feedstuff, in crops and finally, in human foods.

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