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THE GEOCHEMICAL DISTRIBUTION OF HEAVY METALS FOR SOME MINE TAILINGS FROM THE FUNDU MOLDOVEI AREA, ROMANIA

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Abstract: The objectives of the present study were **(i)** to determine the contents of heavy metals (Cr, Cu, Mn, Zn, Cd, Pb, Co, As, Ni and Fe) from tailings samples which had previously been dissolved with HNO_3 and concentrated $HClO_4$, **(ii)** to determine the pH of the samples in both aqueous and saline suspensions, **(iii)** to determine the Eh of the samples, and **(iv)** to calculate the correlation factors between the heavy metal concentration values and the pH and Eh values. The study was conducted on a series of 31 samples, collected from three mine tailings (MT) locations in the Fundu Moldovei area (Dealu Negru and, for the comparison of values, Praşca I and Praşca II). The concentrations of heavy metals were determined by means of Atomic Absorption Spectrometry, after having previously treated the samples with HNO_3 and concentrated $HClO_4$. The pH was determined through the potentiometric method, in both aqueous and saline solution. The data obtained was summed up and projected onto concentration maps and 3D distribution diagrams, both for each minor element, and for the pH and Eh. The concentration maps and 3D diagrams were built by using Golden Software's Surfer 9.7.543 and Visual Basic scripts applied to it. The approximated 3D surface of the mine tailings was obtained, through the same software, only in the case of the Dealu Negru MT, while the other 2 mine tailings deposits were used only in order to compare the values of heavy metal concentrations, pH and Eh. The results have shown that, in case of the Dealu Negru MT, there is a clear discrepancy between the contents of heavy metals from the samples gathered from the top of the mine tailings deposit and the ones collected from the bottom. A possible explanation for this phenomenon would be the presence of a draining pool on top of the Dealu Negru MT, draining pool which was dried out some 5 years ago. For the Dealu Negru MT, the pH values determined in aqueous solution ranged from 2.45 to 5.25, while the Eh ranged from 0.247 V to 0.390 V. For the Praşca II MT, the pH determined in aqueous solution ranged from 3.44 to 4.60, and the Eh ranged from 0.340 V to 0.412 V, while in case of the Praşca I MT, the pH values determined in aqueous solution ranged from 3.73 to 5.12, and the Eh values ranged from 0.280 V to 0.405 V.

Keywords: tailings, heavy metals, pH, Eh, distribution, correlations

1. INTRODUCTION

Among the human activities which have a major impact on the soil are the mining activities, including excavations, ore processing and treatment, when significant quantities of mine tailings are produced, bearing large quantities of heavy metals (Dițoiu & Oşean, 2007).

Given its position, nature and the role it plays as part of the environment, the soil is also an important component of the biosphere, and a product of the interaction between the biotic and the non-biotic environment, representing a specific zone of accumulation of living organisms, energy, and products of metabolism and decomposing processes. The soil represents the primary source of nutrients and energy and, unfortunately, it is inextensible and non-producible. Therefore, the protection of this vital resource and the preservation of its basic functions unaltered constitute an imperative, being one of the major concerns of the modern society.

The presently-ceased mining activities have left a heavy legacy upon the shoulders of the environment, consisting of great amounts of abandoned mine tailings, which, sooner or later, have to be dealt with. Recent studies regarding the soil pollution from dumps located in mining areas have been carried out by Damian et al. (2008a, 2008b), Horaicu et al. (2010), Stumbea (2010). Nagy-Korodi et al. (2011).

The present study was conducted on a series of 31 samples, collected from three mine tailings locations in the Fundu Moldovei area, where stratiform metallic sulphide ore deposits have previously been exploited (Dealu Negru and, for the comparison of values, Praşca I and Praşca II).

2. GENERAL ASPECTS

2.1. Geological setting

The village of Fundu Moldovei (Fig. 1) is situated in the western part of Suceava County, Romania, in the hollow formed by the slopes of Obcina Mestecăniş, fragmented by the tributaries of the river Moldova. It is crossed by the $47^{0}30'$ N parallel and the $25^{0}15'$ E meridian.

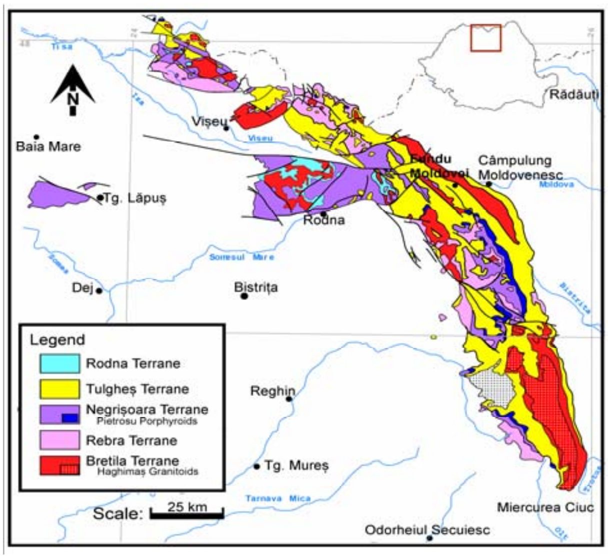

Figure 1 – Location of the village of Fundu Moldovei (modified from Balintoni, 2010)

From a geological point of view, the studied area is located within the Tulgheş metamorphic unit (Lesu Ursului sub-unit) from the Crystalline-Mesozoic Zone of the Eastern Carpathians. The Tulgheş metamorphic unit is the major Mn producer in Romania, and it represents a notable percentage of the output of Pb, Zn, Cu and pyrite, as well as of barite (Balintoni, 2010).

The Tulgheş metamorphic unit, accumulated during the Ordovician, was divided into four "formations", namely (from bottom to top) the Căboaia sub-unit (Tg1) - Quartzitic formation, the Holdiţa sub-unit (Tg2) - Quartzitic-graphitic formation, the Lesu Ursului sub-unit (Tg3) - Volcano-sedimentary rhyolitic formation, and the Arşiţa Rea sub-unit (Tg4) - Phyllitic-quartzitic formation (Vodă & Balintoni, 1994). The Lesu Ursului sub-unit consists of a sedimentary volcanogenic sequence which contains significant accumulations of stratiform metallic sulphides (Balintoni, 2010).

2.2. The Dealu Negru and Praşca II mine tailings

The stratiform metallic sulphide ore from the Dealu Negru mining sector was processed at the Fundu Moldovei ore processing station, in order to obtain copper and pyrite concentrate. The tailings which resulted from the processing station were then deposited at the Dealu Negru draining pool (Ionce, 2010), which ceased its activity in 2001.

The Praşca II mine tailings resulted from the mining activity that extracted the pyrite and copper ore from the Valea Putnei-Praşca accumulation. The locations of all three mine tailings deposits studied are presented in figure 2.

2.3. The Praşca I mine tailings

Praşca I represents another place of deposition for the tailings which resulted from the mining activity in the Valea Putnei-Praşca mining sector. In 2004, the mining perimeter ceased its activity. Afterwards, the rather small tailings of Praşca I were used to deposit construction materials and chopped-down trees that were later used in the lumber industry.

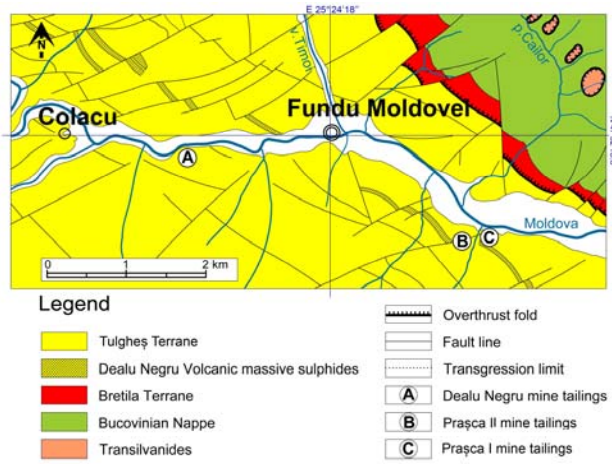

Figure 2 – Locations of the Dealu Negru, Praşca II and Praşca I mine tailings (modified from Petrescu et al., 1975)

3. SAMPLES AND ANALYTICAL METHODS

3.1. Sampling stage and sample preparation

For the present study, we have collected a series of 31 samples (Table 1) from the three above-mentioned mine tailings deposits, as follows:

- Dealu Negru: 22 samples (A1 to A22)
- Praşca II: 5 samples (B1 to B5)
- Praşca I: 4 samples (C1 to C4)

The last two mine tailings deposits were sampled for comparison reasons. The location of each sample is presented in figures 3 to 5.

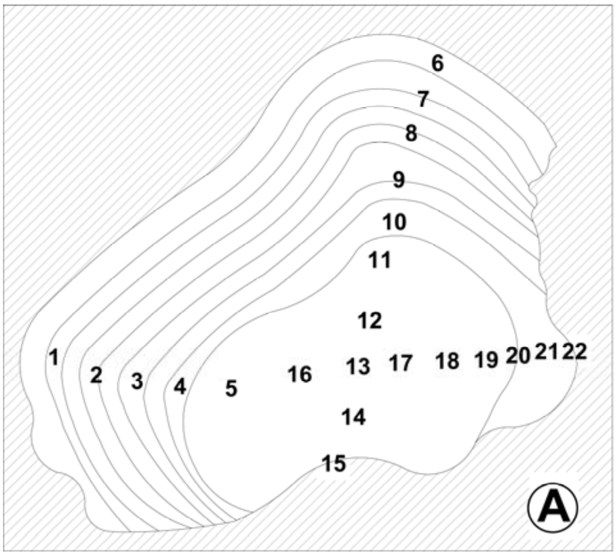

Figure 3. The sampling points within the Dealu Negru mine tailings perimeter (top view)

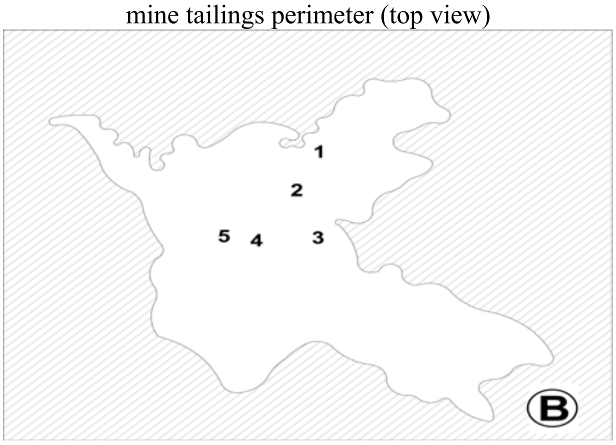

Figure 4. The sampling points within the Praşca II mine tailings perimeter (top view)

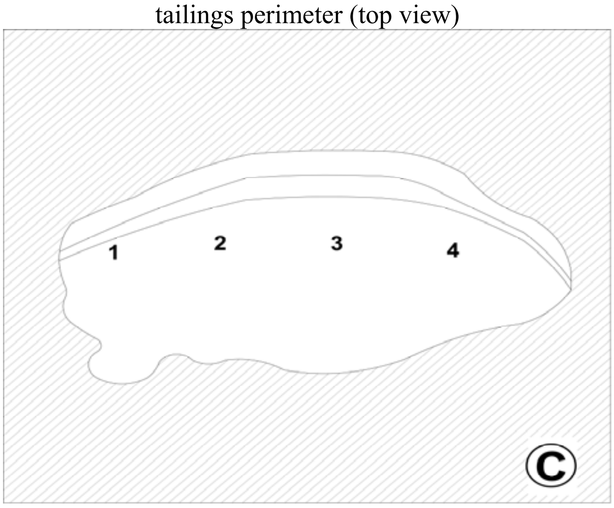

Figure 5. The sampling points within the Praşca I mine tailings perimeter (top view)

Table 1 – Numbers attributed to the samples (No.), geographical coordinates, altitude (Alt.) and weight (m)

No.	Geographical coordinates						Alt. [m]	m [g]
	N Latitude			E Longitude				
	°	\`	\`\`	°	\`	\`\`		
A1	47	32	7,40	25	22	39,13	783	2360
A2	47	32	7,13	25	22	40,26	789	2102
A3	47	32	7,05	25	22	41,28	810	2032
A4	47	32	6,98	25	22	42,29	821	2022
A5	47	32	6,96	25	22	43,57	825	2275
A6	47	32	12,42	25	22	48,77	787	2186
A7	47	32	11,76	25	22	48,39	793	1994
A8	47	32	11,17	25	22	48,03	802	2175
A9	47	32	10,39	25	22	47,68	809	2124
A10	47	32	9,67	25	22	47,36	820	1952
A11	47	32	9,04	25	22	46,98	827	2396
A12	47	32	8,07	25	22	46,67	825	2003
A13	47	32	7,34	25	22	46,36	825	2006
A14	47	32	6,56	25	22	46,24	825	2083
A15	47	32	5,86	25	22	45,77	823	1909
A16	47	32	7,21	25	22	44,97	825	2263
A17	47	32	7,40	25	22	47,38	825	1902
A18	47	32	7,43	25	22	48,47	825	2143
A19	47	32	7,45	25	22	49,39	825	2491
A20	47	32	7,40	25	22	50,29	823	1837
A21	47	32	7,39	25	22	50,80	818	1957
A22	47	32	7,41	25	22	51,30	815	2303
B1	47	31	34,29	25	25	40,50	795	2584
B2	47	31	33,16	25	25	39,74	804	2357
B3	47	31	31,75	25	25	40,40	810	2188
B4	47	31	31,70	25	25	38,38	822	2345
B5	47	31	31,80	25	25	37,40	826	2465
C1	47	31	38,60	25	25	51,60	769	2219
C2	47	31	38,76	25	25	53,67	765	2398
C3	47	31	38,79	25	25	56,20	768	2233
C4	47	31	38,41	25	25	58,26	767	2445

The sampling operation was performed with a manual drill-type soil sampler, using the methods described in the literature (Borlan & Răuță, 1981; Clichici & Stoici, 1986; Florea et al., 1986). The samples were then dried under normal atmospheric conditions for 3 days, and then in the oven, at 40-50^{0}C, for 8 hours. From the dried samples, we eliminated the coarse fractions (Φ > 2.00 mm) and removed the traces of vegetation found in different stages of decomposition. The granulometric fraction which had less than 2 mm in diameter was then grinded, first in an agate grinder, and then in a „Fritz" planetary mill, for 60 minutes, at a speed of 200 rpm. (Clichici & Stoici, 1986), until a granulometric diameter of less than 0,01 mm was achieved.

3.2. pH and Eh determinations

The pH was determined by using the potentiometric method, in both twice-distilled water and 0.1N KCl solution: 10 g of sample for 50 mL of solution, with a contact time of 30 minutes, at room temperature. For the determinations, we used a “pH-Meter Basic 20+” and a couple of electrodes: calomel (as reference) and a pH-measuring electrode.

The redox potential was determined directly, using the process of suspension in twice-distilled water: 10 g sample for 50 mL of water and a contact period of 45 minutes. For the Eh determinations, we used a “pH-100” potentiometer and a couple of electrodes: platinum and calomel (for reference) (Florea et al., 1986; Bloom, 2000).

3.3. Atomic Absorption Spectrometry

The contents of heavy metals from the mine tailings was determined by Lăcătuşu R. at ICPA Bucharest through Atomic Absorption Flame Spectrometry (Atomic Absorbtion Spectrometer model Vario 6FL, with monoelement lamp). The samples were initially dissolved in concentrated HNO_3 and concentrated $HClO_4$ (Borlan & Răuță, 1981).

1 – 5 g of sample (medium samples) were treated at room temperature (for aproximately 4 hours) with 10 mL of concentrated HNO_3 and then on sand-bath at 250-300^{0}C until dry; the obtained residuum was retreated with 5 mL of HNO_3 and 5 mL of $HClO_4$ 2%. Then, the acidic extract was filtered and brought to a 100 mL flask with twice distilled water. The determination of heavy metals was done directly (without any pretreatments - masking or preconcentration).

3.4. Data processing

The interpretation of the geochemical data regarding the distribution of heavy metals (Cr, Cu, Mn, Zn, Cd, Pb, Co, As, Ni and Fe) for the Dealu Negru Mine Tailings was made by using Golden Software’s Surfer 9.7, kriging method, liniar variogram model (Warrick et al., 1986).

The graphical representations of the 3D distribution of heavy metals use a tailings’ morphology that is estimated from the geographical coordinates and the elevation of the sampling points. The correlation matrices were obtained by using StatSoft’s Statistica 8.0.

4. RESULTS AND DISCUSSIONS

The results of the completed analysis on the 31 tailings samples are summed up in tables 2 to 5, showing the contents determined by AAS for each heavy metal, Eh, pH_{aq} and pH_{KCl} and in Figures 6 to 18, showing a computer processed distribution map for the Dealu Negru mine tailings, for each analyzed heavy metal and for the values of Eh, pH_{aq} and pH_{KCl}.

Table 2. The Zn, Cu, Fe and Mn contents [mg/kg] for the samples collected from the Dealu Negru, Praşca II and Praşca I mine tailings*

No.	Zn	Cu	Fe	Mn
A1	102,00	37,30	45964,00	392,00
A2	137,00	81,00	49648,00	740,00
A3	74,00	35,50	33577,00	352,00
A4	327,00	7,08	63571,00	336,00
A5	116,00	17,80	65642,00	220,00
A6	79,00	68,70	29937,00	363,00
A7	127,00	40,10	37500,00	529,00
A8	59,00	29,50	22135,00	262,00
A9	53,00	25,00	26237,00	154,00
A0	117,00	109,00	58429,00	267,00
A11	343,00	1060,00	52361,00	95,80
A12	259,00	549,00	65068,00	216,00
A13	306,00	881,00	59961,00	169,00
A14	229,00	1148,00	49411,00	136,00
A15	884,00	1832,00	74761,00	128,00
A16	228,00	1082,00	74529,00	130,00
A17	204,00	816,00	49468,00	164,00
A18	344,00	1732,00	60309,00	105,00
A19	1020,00	1586,00	61077,00	48,70
A20	263,00	1418,00	52168,00	133,00
A21	50,00	34,90	24166,00	98,00
A22	75,00	120,00	44492,00	109,00
B1	140,00	84,80	35396,00	266,00
B2	178,00	151,00	38143,00	240,00
B3	149,00	83,00	32650,00	436,00
B4	294,00	333,00	65585,00	304,00
B5	154,00	39,70	35705,00	172,00
C1	109,00	52,00	26522,00	133,00
C2	150,00	91,00	32057,00	200,00
C3	1107,00	78,80	36779,00	233,00
C4	126,00	39,70	35133,00	140,00

* Analyses carried out by Lăcătuşu R. at ICPA Bucharest

4.1. The heavy metal contents and the pH values for the Dealu Negru mine tailings

Based on the correlation matrix in table 4, it can be seen that Zn correlated stongly and positively with Pb, Cd and Cu had a less strong positive correlation with Fe, Co, As and Cr. Negative correlations with Zn have been obtained for Mn and Ni. Generally, the Zn content decreased with the increase of the pH values. The average content of Zn for all the mine tailings samples was 245.27 mg/kg. The Zn contents ranged between 50.00 mg/kg (sample A21) and 1020 mg/kg (sample A19).

Table 3. The Pb, Ni, Co, Cr, Cd and As contents [mg/kg] for the samples collected from the Dealu Negru, Praşca II and Praşca I mine tailings*

No.	Pb	Ni	Co	Cr	Cd	As
A1	123,0	67,90	10,30	12,60	1,03	17,70
A2	194,0	37,10	10,40	4,02	1,15	19,40
A3	116,0	35,40	10,20	3,58	1,04	9,53
A4	237,0	37,10	15,30	7,13	1,57	6,98
A5	265,0	40,80	23,20	5,53	1,33	7,45
A6	79,0	33,40	7,78	3,76	1,21	10,80
A7	152,0	33,60	9,13	4,03	1,36	8,01
A8	69,0	34,90	7,50	3,84	1,29	11,40
A9	56,0	30,60	8,63	4,29	1,32	11,30
A10	255,0	35,80	13,70	4,54	1,49	7,09
A11	1932,0	23,50	10,60	22,00	1,84	20,40
A12	1080,0	16,50	5,84	8,68	1,46	11,40
A13	1687,0	10,90	9,76	9,10	1,84	19,80
A14	1324,0	8,76	5,99	6,13	1,76	7,50
A15	2339,0	10,90	12,60	5,70	2,21	11,10
A16	1015,0	10,00	10,10	6,29	1,84	14,60
A17	1355,0	8,79	5,94	2,57	1,92	20,70
A18	1185,0	8,86	8,31	5,97	2,50	10,80
A19	2057,0	13,80	17,90	4,02	2,29	16,40
A20	354,0	12,40	18,00	13,30	2,34	13,90
A21	46,0	31,70	8,02	4,91	1,40	10,20
A22	173,0	32,60	10,50	6,71	1,54	11,00
B1	92,2	14,10	5,03	10,90	2,49	6,22
B2	357,0	8,90	3,36	4,17	2,67	8,34
B3	22,6	31,70	19,50	20,30	2,68	5,03
B4	29,7	27,40	10,10	17,08	2,79	2,94
B5	135,0	14,40	7,24	17,21	2,68	10,70
C1	47,1	8,27	2,91	2,04	2,09	7,92
C2	110,00	9,03	4,77	4,94	2,24	9,83
C3	129,00	29,02	4,33	7,58	2,38	5,76
C4	31,50	10,30	3,73	4,97	2,51	4,03

* Analyses carried out by Lăcătuşu R.

Table 4 – The correlation matrix between the heavy metal contents, Eh and pH determined in both aqueous (pH_{aq}) and saline (pH_{KCl}) suspensions, from the Dealu Negru mine tailings samples

	Zn	Cu	Fe	Mn	Pb	Ni	Co	Cr	Cd	As	Eh	pH $_{(aq)}$	pH $_{(KCl)}$
Zn	1,00	0,76	0,58	-0,38	0,81	-0,50	0,33	0,08	0,70	0,20	0,54	-0,52	-0,56
Cu	0,76	1,00	0,58	-0,57	0,84	-0,80	0,08	0,26	0,93	0,29	0,75	-0,70	-0,77
Fe	0,58	0,58	1,00	-0,22	0,61	-0,41	0,42	0,21	0,55	0,11	0,65	-0,73	-0,69
Mn	-0,38	-0,57	-0,22	1,00	-0,51	0,57	-0,08	-0,23	-0,64	0,00	-0,76	0,75	0,76
Pb	0,81	0,84	0,61	-0,51	1,00	-0,71	-0,01	0,28	0,72	0,42	0,70	-0,67	-0,72
Ni	-0,50	-0,80	-0,41	0,57	-0,71	1,00	0,15	0,02	-0,80	-0,16	-0,70	0,63	0,70
Co	0,33	0,08	0,42	-0,08	-0,01	0,15	1,00	0,12	0,20	-0,15	0,23	-0,36	-0,33
Cr	0,08	0,26	0,21	-0,23	0,28	0,02	0,12	1,00	0,20	0,40	0,45	-0,44	-0,42
Cd	0,70	0,93	0,55	-0,64	0,72	-0,80	0,20	0,20	1,00	0,20	0,80	-0,78	-0,82
As	0,20	0,29	0,11	0,00	0,42	-0,16	-0,15	0,40	0,20	1,00	0,25	-0,15	-0,18
Eh	0,54	0,75	0,65	-0,76	0,70	-0,70	0,23	0,45	0,80	0,25	1,00	-0,96	-0,95
pH $_{(aq)}$	-0,52	-0,70	-0,73	0,75	-0,67	0,63	-0,36	-0,44	-0,78	-0,15	-0,96	1,00	0,98
pH $_{(KCl)}$	-0,56	-0,77	-0,69	0,76	-0,72	0,70	-0,33	-0,42	-0,82	-0,18	-0,95	0,98	1,00

Table 5 – The values of Eh determined in aqueous suspension, and pH determined in both aqueous (pH_{aq}) and saline (pH_{KCl}) suspensions

Sample	Eh[V]	pH_{aq}	pH_{KCl}
A1	0,285	4,61	4,06
A2	0,247	5,25	4,32
A3	0,251	5,25	4,37
A4	0,414	3,15	3,10
A5	0,389	3,03	2,74
A6	0,260	5,04	3,99
A7	0,250	5,19	4,10
A15	0,501	2,74	2,38
A16	0,526	2,47	2,30
A17	0,435	3,42	3,01
A18	0,424	3,05	2,72
A19	0,460	2,93	2,56
A20	0,522	2,45	2,27
A21	0,410	4,01	3,60
A22	0,415	3,56	3,08
B1	0,355	4,13	3,57
A8	0,292	4,84	3,82
A9	0,308	4,14	3,49
A10	0,341	3,51	3,32
A11	0,508	2,51	2,30
A12	0,430	3,34	3,06
A13	0,476	2,61	2,39
A14	0,425	3,18	2,80
B2	0,412	3,44	3,06
B3	0,340	4,60	4,37
B4	0,375	3,51	3,29
B5	0,350	4,01	3,65
C1	0,392	3,90	3,16
C2	0,320	4,85	3,64
C3	0,280	5,12	5,05
C4	0,405	3,73	3,31

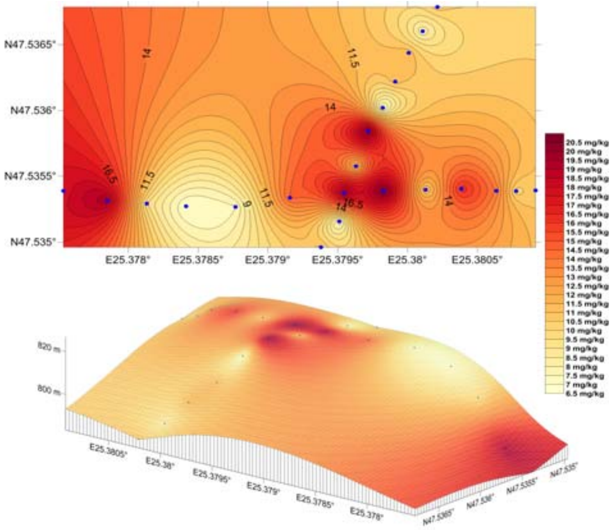

Figure 6 – The distribution of the As contents in the Dealu Negru mine tailings

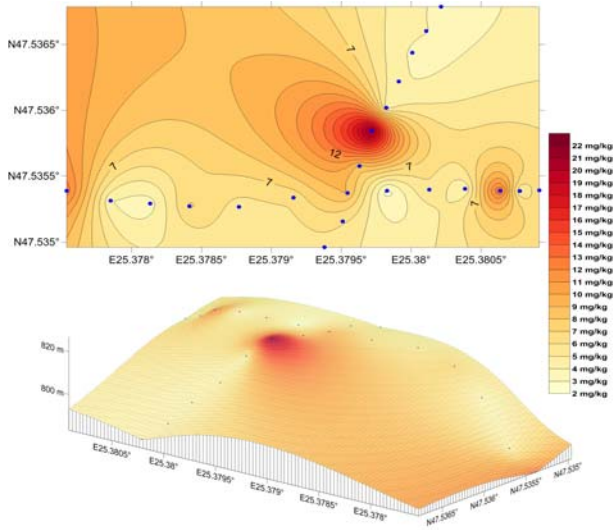

Figure 9 - The distribution of the Cr contents in the Dealu Negru mine tailings

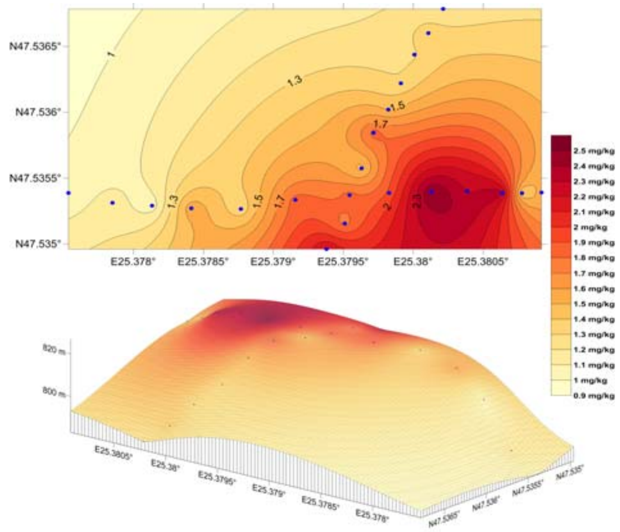

Figure 7 - The distribution of the Cd contents in the Dealu Negru mine tailings

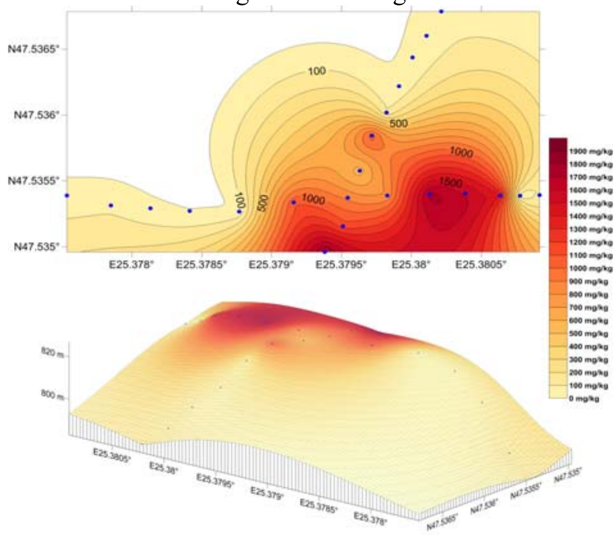

Figure 10 - The distribution of the Cu contents in the Dealu Negru mine tailings

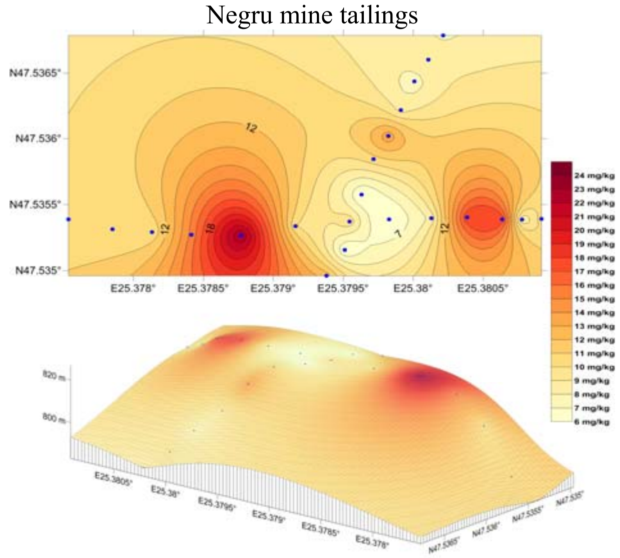

Figure 8 - The distribution of the Co contents in the Dealu Negru mine tailings

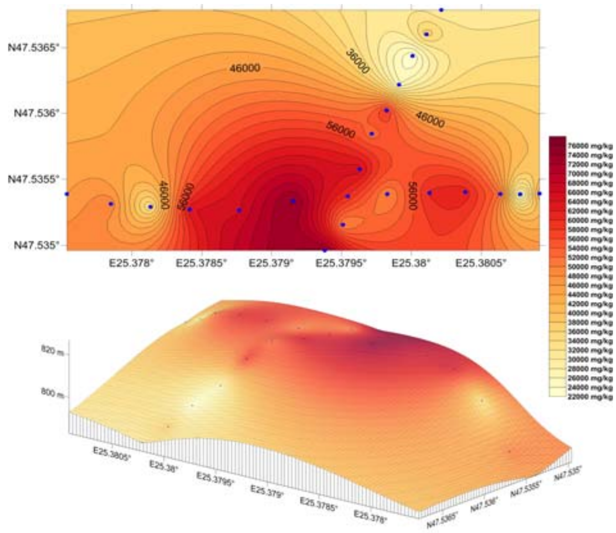

Figure 11 - The distribution of the Fe contents in the Dealu Negru mine tailings

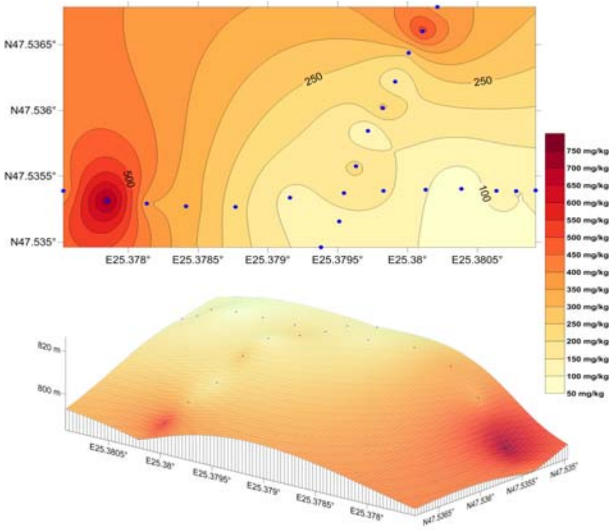

Figure 12 - The distribution of the Mn contents in the Dealu Negru mine tailings

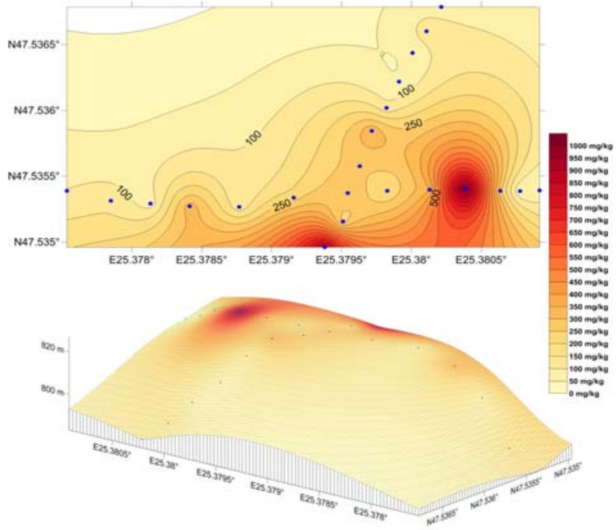

Figure 15 - The distribution of the Zn contents in the Dealu Negru mine tailings

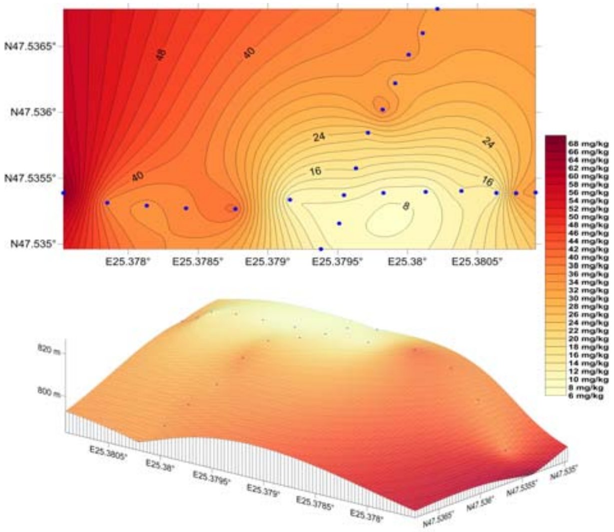

Figure 13 - The distribution of the Ni contents in the Dealu Negru mine tailings

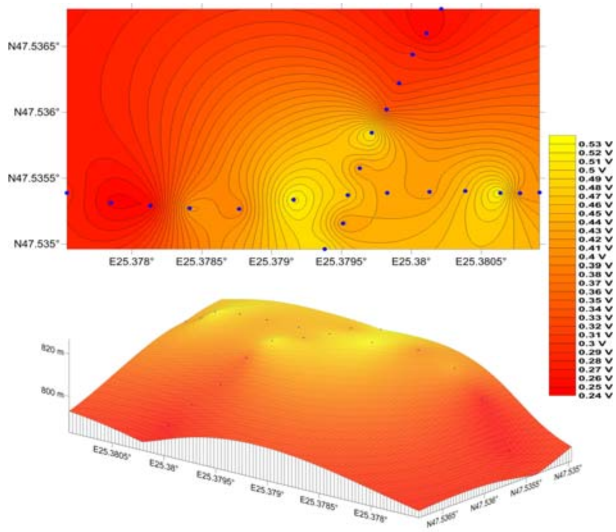

Figure 16 - The distribution of the Eh values in the Dealu Negru mine tailings

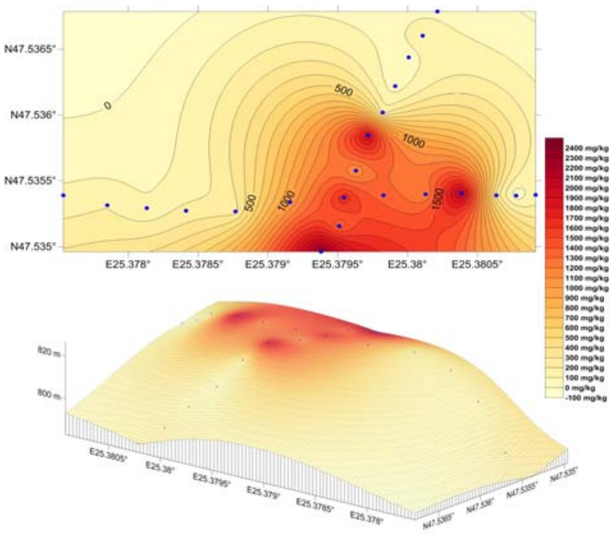

Figure 14 - The distribution of the Pb contents in the Dealu Negru mine tailings

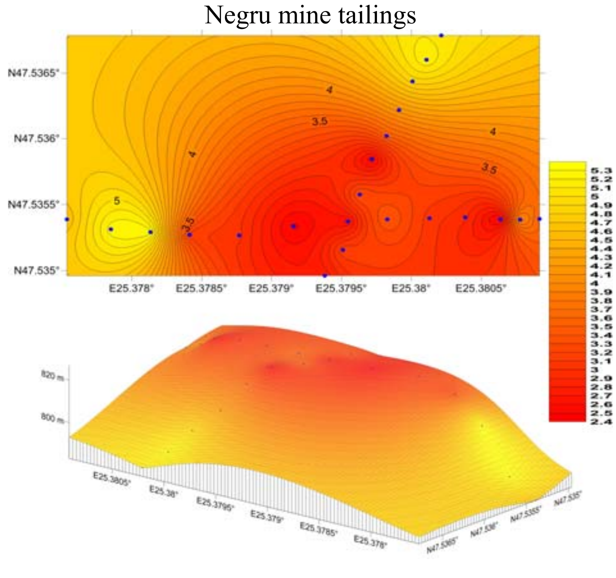

Figure 17 - The distribution of the pH_{aq} values in the Dealu Negru mine tailings

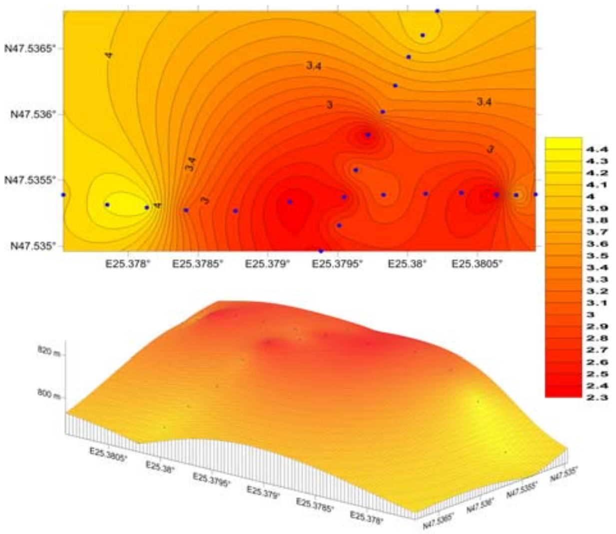

Figure 18 - The distribution of the pH_{KCl} values in the Dealu Negru mine tailings

The Cu contents correlated strongly and positively with Zn, Pb and Cd, and had a less stronger positive correlation with Fe, and a weak correlation with As, Cr and Co. Strong negative correlations with Zn have been obtained for Ni. The Cu content generally decreased with the increase of the pH value. The average content of Cu for the Dealu Negru mine tailings was 577.72 mg/kg, and the values ranged between 7.08 mg/kg (sample A4) and 1832 mg/kg (sample A15).

Fe generally had good geochemical correlations with almost every other element, except Mn, Ni and Cr. The contents of Fe decreased with the increase of the pH values. The average content of Fe for the Dealu Negru mine tailings was 50018.68 mg/kg. The values were between 22135.00 mg/kg (sample A8) and 74761 mg/kg (sample A15).

The correlation factors recorded for Mn are greater than 0.5 only with Ni, having a negative correlation with all the other elements, except As, in which case the correlation factor was null. The Mn contents increased with the increase of the pH. The average Mn content was of 233.98 mg/kg, and the content values ranged between 38.70 mg/kg (sample A19) and 740 mg/kg (sample A2).

Pb had strong positive geochemical correlations with Zn, Cu and Cd, and strong negative correlations with Ni. The Pb contents have generally decreased with the increase of the pH. The average concentration of Pb for the Dealu Negru mine tailings was 731.50 mg/kg. The contents were between 46.00 mg/kg (sample A21) and 2339.00 mg/kg (sample A15).

Ni correlated weakly with Mn and Co, but had strong negative geochemical correlations with Cu, Cd and Pb. Ni did not significantly correlate with Cr. The Ni contents increased with the increase of the pH value. The average content of Ni for the Dealu Negru mine tailings was of 26.15 mg/kg, the contents ranging between 8,76 mg/kg (sample A14) and 67,90 mg/kg (sample A1).

Co had weak positive correlations with Zn, Cu, Fe, Ni, Cr, Cd, and weak negative correlations with Mn, Pb and As. The content of Co had a slight tendency to increase with the decrease of the pH. The average content of Co for the Dealu Negru mine tailings was of 10.90 mg/kg, and the contents ranged from 5.84 mg/kg (sample A12) to 23.20 mg/kg (sample A5).

Cr had weak correlations with all the other elements. The content of Cr decreased as the pH values increased. The average content of Cr in the Dealu Negru samples was of 6.76 mg/kg, while the contents ranged from 2.57 mg/kg (sample A17) to 22.00 mg/kg (sample A11).

Cd geochemically correlated strongly and positively with Cu, Zn and Pb, had a good positive correlation with Fe, a weak positive correlation with Cr, Co and As, and a strongly negative correlation with Mn and Ni. The content of Cd decreased with the increase of the pH values. The average content of Cd was 1.62 mg/kg. The Cd content ranged from 1.03 mg/kg (sample A1) to 2.50 mg/kg (sample A18).

As had a positive correlation with Pb and Cr. It also correlated positively, but weakly, with Fe and Cd, while having a null correlation factor with Mn. The average As content was 12.61 mg/kg, with contents ranging between 6.98 mg/kg (sample A4) and 20.70 mg/kg (sample A17).

The very high correlations between the values of the pH determined in aqueous suspension and the values of pH determined in saline suspension sustain the hypothesis of correct and conclusive analyses.

As far as the pH and Eh are concerned, it can be stated that for the Dealu Negru mine tailings there was a notable discrepancy between the values determined for the samples gathered from the slopes of the tailings deposits, and the values determined for those collected from the top of the mine tailings. This phenomenon is probably caused by the presence of a draining pool on top of the tailings, pool which was dried out aproximately 5 years ago through the use of auxiliary draining pipes. This also explains the high contents of Fe, Zn and Pb in the samples gathered from that section of the mine tailings deposit.

Generally, the increasing acidity was associated with the presence of high concentrations of Pb, Cd, Cu, Fe and Zn, and relatively low concentrations of Mn and Ni. These two groups of heavy metals were obviously nagatively correlated.

For the Dealu Negru mine tailings, the pH analysis in aqueous suspension rendered an average pH of 3.65, with values ranging from 2.45 (sample A20) to 5.25 (sample A5). As far as the redox potential is concerned, the average value is 0.390 V, the maximum value of 0.526 V having been obtained for Sample A16, and the minimum value being 0.247 V (sample A2).

4.2. The heavy metal contents and the pH values for the Praşca II

In the case of the Praşca II mine tailings, the minimum pH value determined in aqueous suspension was 3.44 (sample B2), while the maximum value was 4.60 (B3). The average pH in the case of the Praşca II mine tailings was 3.94.

The redox potential values had an average of 0.366 V, with a minimum of 0.340 V (sample B3) and a maximum of 0.412 (sample B2).

4.3. The heavy metal contents and the pH values for the Praşca I mine tailings

For the Praşca I mine tailings, the pH values determined in aqueous solution ranged from 3.73 (sample C4) to 5.12 (sample C3). The average pH was 4.40.

The values of the redox potential determined in aqueous solution for the samples collected from the Praşca I mine tailings had an average of 0.394 V, ranging from 0.280 V (sample C3) to 0.405 (sample C4).

Due to the small number of samples, a correlation matrix was considered irrelevant and unnecessary in case of the Praşca I and Praşca II mine tailings.

5. CONCLUSIONS

In the heavy metal distribution, a certain discrepancy was observed between the contents from the samples gathered from the slopes and the samples collected from the top of the tailings deposit.

The differences between the values of the pH determined in aqueous and saline suspensions show that, generally, amorphous minerals have a reduced contribution to the acido-basic reaction of the mine tailings studied. There are, however, some samples that gave a $|pH_{aq} - pH_{KCl}|$ difference higher than 1, indicating a more consistent contribution of amorphous minerals to the acido-basic reaction.

Taking into account the fact that the redox potential for the studied samples is relatively low (very close to the reductive domain), it can be stated that the redox potential in the case of the mine samples studied is mostly controlled by the equilibriums between the speciation forms of sulphur.

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