MINERALOGY AND GEOCHEMISTRY OF THE TAILINGS POND FROM STRAJA VALLEY (SUCEAVA COUNTY, ROMANIA). FACTORS AFFECTING THE MOBILITY OF THE ELEMENTS ON THE SURFACE OF THE WASTE DEPOSIT

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Abstract: The present study focuses on the physical, mineralogical and geochemical characterization of the tailings pond from Straja Valley, resulted from the now abandoned ore-processing plant of Tarniţa (Ostra). In terms of granulometry, around 70% of waste material consists of fine and very fine particles. The sulfides of the waste are pyrite, subordonate sphalerite and very rare galena. The silicates consist mainly of quartz and sericite, subordinate chlorite, feldspars; accidentally, also barite was identified within the waste. The salt crusts occur on some areas of the surface of the tailings pond. They consist mainly of mineral species of the alunite-jarosite solid solution series (i.e., jarosite, hydronium jarosite, plumbojarosite and alunite). However, small amounts of gypsum (detected significant only in white crust) and copiapite were also identified, as well as clay minerals (i.e., kaolinite and illite), formed through the weathering of silicates. All samples from the beach and dam of the tailings pond display a high acidity (pH mean of 2.81) and relative high amounts of water soluble fraction (mean of 9.71 wt%). The most abundant major elements are Si, Fe and Al; the decreasing sequence of abundance is the following: Si>Fe>Al>K>Mg>Na>Mn. The most abundant minor elements are Pb, Zn, Cu and As, whom sequence of abundance is Pb>Zn>Cu>As>Cr>Co>Cd. According to the particle size of the waste, some of elements (e.g. Fe, Mn, Cu, Zn, As) have a high affinity for the fine and very fine particles, being rather concentrated in the silt and clay fractions than within the arenite fractions. Multivariate statistics revealed four distinct types of waste, as well as three factors that control the distribution of the chemical elements: 1) water soluble fraction, 2) pyrite abundance; 3) Ca-bearing minerals. Moreover, the rainfall regime and morphology of the waste deposit also seem to influence the mobility and accumulation of both major and minor elements on the surface of the tailings pond. In terms of environmental pollution, the fine and very fine particles, which accumulate very high amounts of minor and major elements, are susceptible to be transported towards the surrounding areas by wind or water, during rainfall. During the latter events, the acidic leachates, highly enriched in toxic elements, were mobilized by runoff, thus reaching the neighborhoods of the waste deposit.

Keywords: acid mine drainage (AMD), tailings pond, toxic elements, environmental pollution, GIS, multivariate statistics.

1. INTRODUCTION

Mining and ore-processing activities produce vast quantities of waste that can have severe and widespread impacts on environment over a long period of time. The most significant environmental issue associated to mining activities is the acid mine drainage (AMD), which is generated by the oxidation of sulfides (particularly pyrite) under subaerian conditions (Nordstrom, 1982; Nordstrom & Alpers,

1999; Moncur et al., 2009). AMD is low-pH water that usually contains Fe (II), Fe (III) and SO_4 as well as high concentrations of dissolved toxic elements (Moncur et al., 2005; Romero et al., 2007; Parviainen, 2009; Lindsay et al., 2015). The acid solutions enrichment in toxic elements from the mining perimeters represents a considerable source of pollution for soils, sediments, and surface waters. The secondary minerals phases which were formed either through precipitation or evaporations of AMD (Dold & Fontboté, 2001), play also an important role in the acid mine drainage due to their capacity for the sequestration of minor elements (Hammarstrom et al., 2005; Romero et al., 2007). Moreover, the secondary minerals phases have a higher contribution to the mobility and release of the potentially toxic elements in mine tailings (Savage et al., 2000, Moncur et al., 2005; Romero et al., 2007, Carbone et al., 2013; Nordstrom, 2011). The weathering degree, formation of secondary minerals, as well as mobility of toxic elements in mining perimeters are closely linked to the climatic conditions (Dold & Fontboté, 2001; Hammarstrom et al., 2005).

Ore-processing plants produce large quantities of waste material, such as tailings impoundments that usually result from the crushing and grinding of rock and ore fragments to small size particles, for an increased benefaction (Blowes et al., 2004). Many authors have reported that the small-sized particle in the waste deposit is another parameter involved in the toxic elements mobility because the finer material is more susceptible to be transported to the environment during either rainy or windy periods (Navarro et al., 2008; Audry et al., 2010; Stumbea & Pavel, 2014; Stumbea, 2013a; 2013b). Therefore, besides the geochemical and mineralogical analyses, the grain size distribution of waste helps in the estimation of environmental risk factors.

The objectives of this work were: (i) determination of grain size fractions; (ii) mineralogical descriptions of the bulk waste material and salt crusts; (iii) a detailed geochemical investigation, performed on salt crusts and on three grain size fractions of the bulk samples; (iv) evaluation of the spatial distribution of major and minor elements across the surface of the waste deposit. Pointing out the physical, mineralogical and geochemical descriptions will allow the identification of the various factors that control the mobility and transport of elements out of the tailings pond. In this respect, the study was conducted so as to assess the most susceptible areas of the tailings pond from Straja Valley to release solid materials and leachate into the surrounding environment.

2. GEOLOGY AND STUDY AREA

2.1. Site description

The study area is located on the administrative territory of the Suceava County (Romania), at 6 Km southwest Ostra village (Fig. 1). The tailings pond from Straja Valley is a valley-type impoundment located at about 500 m from the confluence with Brăteasa River, which is a tributary of Suha River. The solid waste deposit covers an area of 10ha approximately; it has a height of 30m, a length of 500 m and a maximum width of 250 m. As a result of rainfall, a water pool is accumulated in the southeast zone of the beach. At the northwest end, an embankment intended to support the waste material is built (Fig. 1). The unconsolidated dam is characterized by a morphology which leads to a rapid drain of rainfall waters. The tailings have resulted from the Tarniţa processing plant. During its activity from 1950s to 2007, the processing plant of Tarniţa has been aimed to benefit Cu from the Cu±Zn±Pb massive pyrite ore, mined from the metallogenic field of Leşu Ursului (Fig. 2).

2.2. Geology

The polymetallic massive pyrite belt of the Eastern Carpathians displays a NW-SE development, with a length of about 180 km (Kräutner, 1984). The pollymetallic belt is associated with the low-grade metamorphic unit of the Tulghes Group (Balintoni et al., 2009, Balintoni, 1997) (Fig. 2). The Tulgheş Group displays various lithologies, but it consists mainly of two types of rocks: white or black quartzites and quartz-feldspar rocks (Balintoni, 2010).

This group was built up during Cambrian (Iliescu et al., 1983) and was divided by Kräutner (1984) in five units, designated (from bottom to top) as Tg1–Tg5. The significant accumulations of metallic sulfides were associated with Tg3 and are shaped as massive strata, lenses, or bodies with disseminated metallic minerals (Kräutner, 1984, 1988). The ore bodies are associated with quartz-sericite-chlorite schists, quartz-chlorite schists and quartz-sericite schists (Kräutner, 1984; Berbeleac 1988). The ore deposits are concentrated in the following three districts (from N to S): (1) Borşa-Vişeu, (2) Fundu Moldovei - Leşu Ursului, and (3) Bălan-Fagu Cetăţii (Berbeleac, 1988). Kräutner (1984) separated the sulfide ore deposits into three morphologic-depositional types:

(1) Isipoaia type is characterized by lens-shaped ores and typically are settled in Leşul Ursului
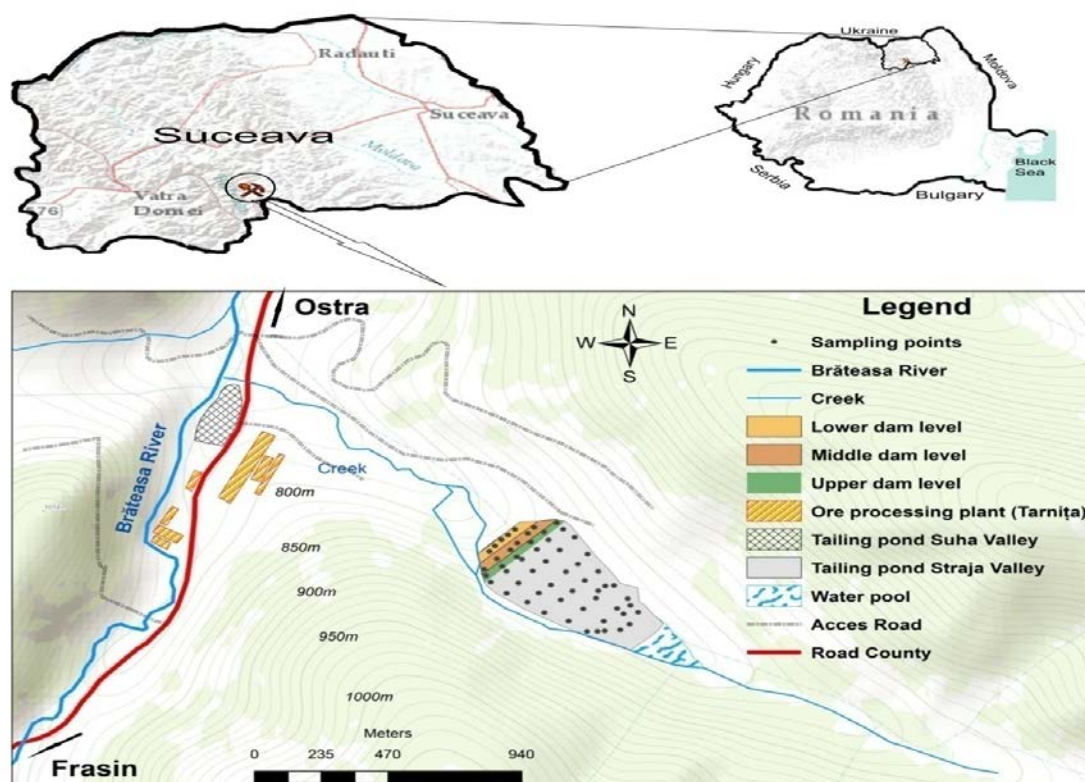
Figure 1. Location of the tailings pond from Straja Valley and the sampling grid.

(zone III-Isipoaia), Fundul Moldovei (zone I) and Baia Borşa (Burloaia) areas. The inner, massive polymetallic pyrite ore is usually surrounded by concentric bands of massive or disseminated ore, sometimes chlorite schists. The lenses display a gradual transition from a central polymetallic ore, throughout a Cu-rich pyrite ore, to a marginal pyrite ore.

(2) Leşul Ursului type consists of a massive polymetallic ore and is only represented by the zone I, Leşul Ursului. It shows a gradual transition from a massive polymetallic ore to a large zone of disseminated ore.

(3) Fundul Moldovei type is composed of disseminated Cu-rich pyrite, developed at Fundul Moldovei (zone II), Leşul Ursului (zone III), and Bălan.

The Leşu Ursului metallogenic field is part of Fundu Moldovei – Leşu Ursului district and lies roughly within the center of the Polymetallic Belt (Fig. 2). It is located in the Bistriţa Mountains, and is associated with the volcano-sedimentary rhyolitic formation – Tg3 (Kräutner, 1984; 1988). This lies between Leşul and Ursul creeks, made up from tree different zones (numbered from I to III) whith NV-SE direction (Petrulian et al., 1966).

The main sulfide minerals of Leşu Ursului metallogenetic field are pyrite, chalcopyrite, sphalerite, galena and subordinate arsenopyrite, pyrrhotite, marcasite, tetrahedrite, bournonite, galenobismutite, molybdenite, semseyite, jamesonite, gold, illmenite, bismuth, magnetite, covellite and cassiterite. Gangue minerals consist mainly of quartz, calcite, ankerite, chlorite, muscovite; subordinate albite and sfen (Petrulian et al., 1966).

3. MATERIALS AND METHODS

3.1. Sampling

The fieldworks were performed during the autumn and summer seasons. During the first campaign, a total of 48 samples of waste material were collected (~2 kg weight each), from the surface of the tailings pond. The sampling procedure resulted in two tailings categories: 1) Samples taken from the upper surface (beach) of the tailings impoundment (31 samples); 2) Samples collected from the dam surface (17 samples). The sampling was performed following a rectangular grid, at regular intervals of 50 × 50 m; all sample points were georeferenced with help of a GPS tracking device. During the second field survey, 9 samples of salt crusts developed on the surface of tailings pond were collected. All samples were collected with the help of a paddle and stored on-site in sealed plastic bags to prevent contamination.
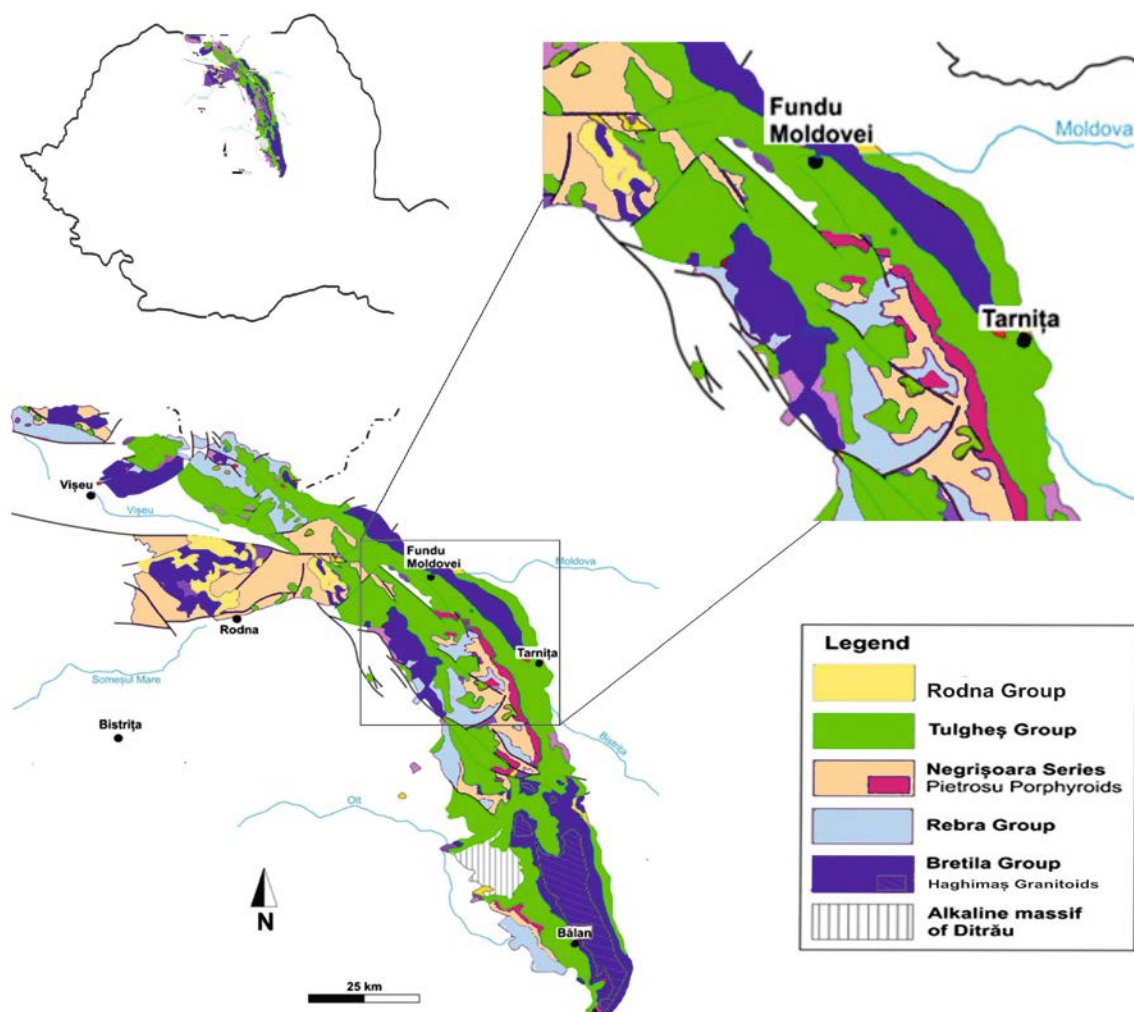
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Figure 2. Geological setting of the Cu-rich pollymetallic belt from the Eastern Carpathians (modified from Balintoni, 2010)

3.2. Analytical procedure

All samples were dried using an electric oven (40ºC), then sieved to remove foreign, organic especially, matter and quartered for general analytical determinations. In order to achieve upright physical-chemical and mineralogical descriptions of the tailings pond from Straja Valley, different analytical methods were applied, which are detailed in the following paragraphs.

3.3. Particle size analyses

In order to identify the particle size of the tailings, a part of the bulk samples was passed through a set of sieves. Thus, weight percent's of four distinct size fractions were determined, as follows: >1 mm, 1–0.25 mm, 0.25–0.063 mm, <0.063 mm.

3.4. X-ray diffraction

Specimens for XRD analysis were separated from the waste samples and salt crusts, being afterwards ground into a fine-grained powder using an agate mortar. The waste and salt crusts samples were analyzed by X ray diffraction (XRD), using a Shimadzu LabX XRD-6000 diffractometer (Cu Kα radiation $\lambda = 1.5406$Å), operating at 40 KV, with a beam current of 30 mA. Scans were recorded from 4 to 80º 2θ, with a step-scan of 0.02º 2θ and a counting time of 0.30 s per step.

3.5. X-ray fluorescence

For chemical studies, a part of the dried sample was ground to a fine-grained powder with an agate mortar, then mixed with Hoechst® wax (ratio of 5:1 sample/binding agent) with help of an agate mill and pressed to pellets at 20 t/cm^2. The chemical composition of the bulk samples and each of the three particle size fractions (<0.063 mm, 0.063 mm-0.25 mm, 0.25 mm – 1 mm) was determined by X-ray fluorescence analysis, with help of energy dispersive EDXRF-spectrometer (Epsylon 5). The

calibration of the spectrometer was based on 24 Certified Reference Materials (STSD1–4, SO1-4, LKSD1–4, Till1–4, JLk1–3, RT, RTH, GSD etc.), including soils and geological materials. The exposure time was 60 s, with the exception of As and Cd, in which case the exposure time was 90 s.

3.6. Leaching tests

During the leaching approach, the pH of the samples was measured using the potentiometric method, at room temperature. The samples were placed in a beaker and immersed in distilled water (1:5 solid/liquid ratios). The mixture was stirred, and then allowed to settle; after a 30 min contact between solid and liquid, the pH was determined with a MeterLab PHM 250 Ion Analyzer – Corning 555.

In order to evaluate the soluble fraction of the waste material, 10 g sample aliquot was mixed with 100 mL of deionized water. The samples were vigorously stirred for fifteen minutes and then filtered through a 0.2 μm cellulose filter. Afterwards, to calculate the percentage of the soluble phase, the insoluble fraction remaining on the cellulose filter was dried and weighed by a precise digital balance with an accuracy of ± 0.01 g.

3.7. Multivariate statistics and spatial analyses

In the last period, multivariate statistical methods have been applied broadly to study different components of the environment, such as soil, sediments, surface water and mine waste as well (Drew et al., 2010; Favas et al., 2011; Acosta et al., 2011; Jiang et al., 2015). In this study however, prior to a multivariate statistical approach, descriptive statistics (mean, minimum, maximum and standard deviation) was performed for all physico-chemical parameters. Next, in order to evaluate quantitatively the relationships among data, multivariate statistics was achieved, i.e., Pearson correlation matrix, hierarchical clusters analysis (HCA) and Principal Component Analysis (PCA). Pearson correlation matrix was used to identify the relationship between the geochemical variables (correlation coefficient, *r*). In order to fulfil the requirements for the use of HCA and PCA statistical models, all variables were log-transformed and then standardized (Güler et al., 2002; Yidana et al., 2008) by calculating their standard scores (*z*-scores) as follows (Eq. 1):

$$Z_i = \frac{(x_i - mean)}{s} \qquad (1)$$

where: Z_i= standard score of the sample i; x_i= value of sample i; s = standard deviation.

The HCA were applied to evaluate whether the samples from the tailings pond are grouped into different populations based on their similarity. Ward linkage method and Euclidean distance were used together, to improve the classification in distinct groups (Güler et al., 2002; Yidana et al., 2008). The PCA helped to reduce the variables of a large initial matrix data (geochemical data) to a few factors (or principal components – PC). The reduction of factors of dataset is accomplished by linear combinations of the variables of the original matrix, which allow making a clear description of the analyzed data. Resulting factors can be presented as scores and weights (Hu et al., 2013; Jiang et al., 2015). Therefore, to facilitate the interpretation, Varimax rotation method was used because the orthogonal rotation minimizes the number of variables and increases the loadings of variables on each factors resulted (Jiang et al., 2015). Both descriptive and multivariate statistical calculations were performed using XLSTAT and NCSS softwares. The mapping and spatial analysis was performed using the ArcGIS v10.1. The interpolation of the data was achieved by the Inverse Distanced Weighted (IDW) interpolation method.

4. RESULTS AND DISCUSSION

4.1. Mineralogy

As pointed out by Dold (2003), a detailed mineralogical study is highly needed in the same time with the geochemical data in mine wastes investigation. Thus, the XRD analysis was applied on two categories of samples, as follow: a) bulk/regular waste; and b) salt crusts. Further, a description of both type of waste is made.

The bulk waste samples revealed that the most abundant mineral is quartz; sericite, chlorite, feldspars and very rare barite were also identified. The frequently identified sulfide minerals are pyrite and minor amounts of sphalerite. Previous observations carried out with help of a stereomicroscope performed on a large number of samples are consistent with the XRD analyses (Chicoş et al., 2014). Also, the detailed microscopic examination revealed that the surface of the primary minerals is covered with smaller secondary mineral grains.

Based on the XRD patterns, three categories of minerals were identified in the salt-rich crust samples (Fig. 3): 1) Primary minerals (e.g., quartz, sericite, pyrite and sphalerite); 2) Secondary minerals of hydrated oxides and sulfates type (e.g., jarosite, alunite and gypsum); 3) Secondary minerals of clay minerals type (i.e., kaolinite and illite).

Generally, the primary minerals that occur in the bulk waste are also present in the crust samples. A relative variety of secondary mineral phases were identified in the salt crusts developed at the surface of the tailings pond Straja Valley. These secondary mineral assemblages consist principally of species that belong to the alunite-jarosite solid solution series; sometimes, they appear associated with variable amounts of gypsum, as well as trace amounts of copiapite. The minerals of the alunite group identified within the study waste are K-jarosite, which is the predominant secondary mineral, hydroniumjarosite and plumbojarosite, but XRD patterns of alunite were also found. Similar accumulations of alunite-jarosite solid solutions have been identified in other AMD related studies (Gunsinger et al., 2006; Smuda et al., 2007; Hayes et al., 2014; Apopei et al., 2014; Buzatu et al., 2016). The alunite–jarosite series includes Fe and Al hydroxyl sulfate minerals $[K(Fe^{+3}/Al^{3+})_3(SO_4)_2(OH)_6]$ (Jambor et al., 2000). However, in acid-drainage environments, jarosite $[KFe_3(SO_4)_2(OH)_6]$ is the most abundant mineral, but different members of the alunite group can also appear: natrojarosite $[NaFe_3(SO_4)_2(OH)_6]$, hydroniumjarosite $[(H_3O)Fe_3(SO_4)_2(OH)_6]$, plumbo-jarosite $[PbFe_6(SO_4)_4(OH)_{12}]$, alunite $[KAl_3(SO_4)_2(OH)_6]$, as well as As-bearing species (Blowes et al., 2004). In low-pH (pH < 3) and sulfate-rich environments, jarosite and hydroniumjarosite can precipitate (McGregor & Blowes, 2002; Crowley et al., 2003). The types of secondary minerals developed in the mine waste are also influenced by the composition of the wastes (Lottermoser, 2003). Thus, the high dissolution of silicates releases significant K^+ in acidic environment, thereby K-jarosite can be supersaturated (Dold & Fontboté, 2001). Therefore, due to the high amounts of alkali-bearing minerals (e.g., sericite, feldspars) and sulfides minerals (e.g. pyrite, galena), where pyrite that generate high acidity is substantial, the tailings pond from Straja Valley is a favorable environment for the precipitation of the jarosite group minerals.

Gypsum $[CaSO_4 \cdot 2H_2O]$ was detected in significant proportions in the white mineral crusts. This secondary mineral occurs frequently associated with other soluble sulfates in most of the mine wastes (Jambor et al., 2000; Hammarstroma et al., 2005).

Copiapite $[Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O]$ was identified in lower amounts in the waste samples. Copiapite is predominant within the mine wastes (Jambor et al., 2000), occurring either in relatively acidic or highly acidic environments (Nordstrom & Alpers, 1999).

In terms of clay minerals, the most abundant mineral is kaolinite $[Al_2Si_2O_5(OH)_4]$, while illite $[(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10})(OH)_2,(H_2O)]$ was identified only in some samples. The dissolution of aluminosilicates (e.g. sericite) leads to the formations of clay minerals (e.g. kaolinite), and K released in the AMD solutions is a source for the formation of jarosite group minerals (Dold & Fontboté, 2001; Bea et al., 2010).
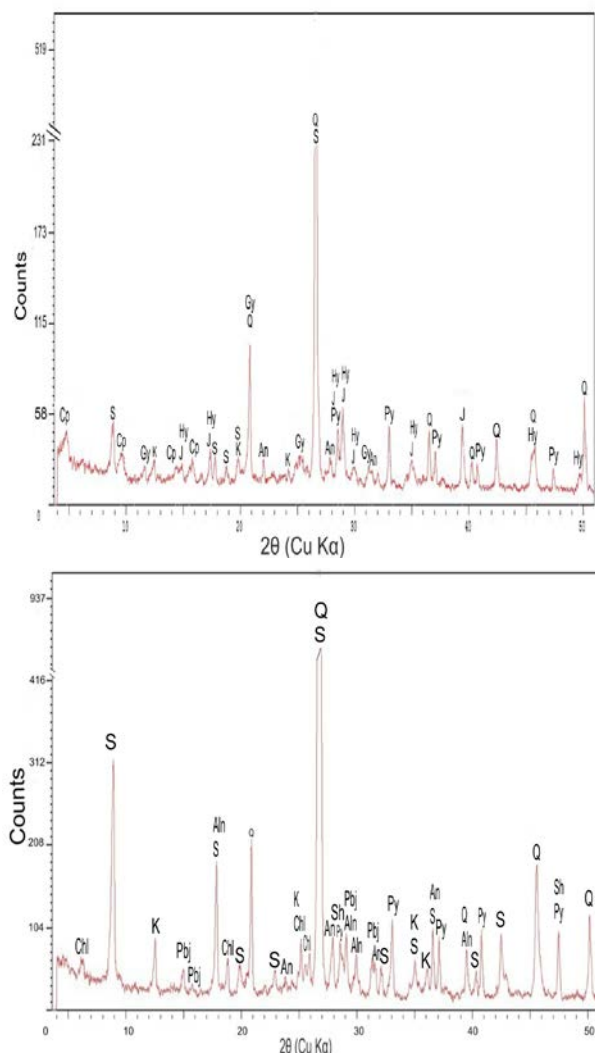
Figure 3. X-ray diffraction patterns of crust samples: J - jarosite; Hy - hidronium-jarosite; Aln - alunite; Pbj - plumbojarosite; Gy - gypsum; Cp - copiapite; K - kaolinite; S - sericite; Q – quartz; Ch - chlorite; An - Anortite; Py - pyrite; Sh - sphalerite.

4.2. Grain size particles

Data regarding the particle size distribution of the studied waste are given in Table 1. From the grain size distribution data it can be seen that the most abundant particles (around 70 % of the mass) are those similar to very fine sand, silt and clay size fractions (smaller than 0.25 mm). The sand-size particles (i.e., larger than 0.25 mm) equal about 30% of the tailings mass. Due to their small size, the sandy

particles, as well as the silt and clay fractions can be removed from the waste deposit either through hydromechanical transport during rainfall events or by wind-borne transport, (Quispe et al., 2013).

Table 1. Grain size analysis (wt%) of the tailings (n = 48)

	> 1	1 - 0.25	0.25 - 0.063	< 0.063
	mm			
Min.	0.00	2.04	25.16	0.00
Max.	31.30	59.45	85.21	47.81
Mean	4.34	23.13	55.02	17.51
SD	6.32	14.88	15.19	12.75

4.3. Geochemistry

4.3.1. Descriptive statistics

The geochemical characterization regarded the waste material from the horizontal surface (beach) of the tailings impoundment, dam area and salt crusts. Tables 2 and 3 present a general summary of the basic statistical parameters of all samples.

Table 2. pH and amount of soluble fraction (SF) of the tailings (n = 57)

	SF (wt %)	pH
Min.	1.48	2.46
Max.	34.73	4.18
Mean	9.75	2.81
SD	6.15	0.32

SF= soluble fraction; SD=standard deviation

The waste material from both beach and flanks of the Straja Valley tailings pond is very acidic, as pH ranging from 2.46 to 4.18 shows (Table 2). Previous studies conducted on similar wastes have led to analogous results (Stumbea & Chicoș, 2012; Stumbea, 2013b). The abundance of the water-soluble fraction within the tailings pond ranges in between very broad limits, i.e., from 1.48 wt% to 34.73wt% (Table 2). The water-soluble fractions in the top of the tailings pond (oxidizing zone) are able to concentrate significant amounts of cations and SO_4 as well as metals (Dold & Fontboté, 2001; Parviainen, 2009). This suggests that during rainfall the waters leaching the surface of tailings pond are able to transport high amounts of cations, sulfates and metals to the environment.

This assumption is supported by previous studies carried out on similar wastes, which showed that the water soluble fraction is controlled by oxidation–precipitation–hydration–dehydration–dissolution processes (Joeckel et al., 2005; Kossoff et al., 2012; Lindsay et al., 2015).

The descriptive statistics of the geochemical composition of the tailings samples is summarized in Table 3. Geochemical characteristics revealed that, as would be expected based on the mineralogy; the dominant major elements of the waste are Si, Fe, and Al. Their sum has highly variable values, but can reach up to 70 wt% of the major elements. According to Table 3, the mean values of major elements contents decrease in the following order: Si >Fe >Al >K >Mg >Na >Mn. The relatively high concentrations of Al, K, Mg, Na and Mn (Table 3) can be associated with the primary minerals (e.g. sericite, chlorite) and secondary minerals as well. Regarding the minor elements, the general order of abundance in the tailings is: Pb >Zn >Cu >As >Cr >Co > Cd.

The concentrations of Pb, Zn, Cu and As (average values of - 1555, 900, 710 and 195 ppm) are very high and vary within very broad limits (Table 3). Cr, Co and Cd did not exhibit high concentrations (average values of 37, 30 and 2 ppm). A notable aspect is that the major and minor elements, excepting Si, Cr and Co, exhibit the enrichment in the salt crusts samples in comparison to the bulk waste materials (Tabel 3).

In order to identify the concentration of the major and minor elements depending on the particle size, the chemical analysis was carried out on each fraction of several samples (Table 3). Main chemical elements (e.g., Al, K, Mg and Na) display a relationship from the point of view of concentrations in each fraction. For instance, their concentrations are approximately constant in the three determined fractions, with a slight tendency to accumulate in the fraction similar to the fine and very fine sand.

This suggests that the concentrations of these elements in each fraction are controlled by the abundance of silicate minerals (e.g., sericite, chlorite) and to a lesser extent of secondary minerals. An aspect to be highlighted is that of Fe content is very high in silt and clay fractions and decrease with the increase of particles size, being two times lower in coarse and medium sand fractions, than in silt and clay fractions. The high concentrations of Fe in the silt and clay fractions may be explained as follow: (1) the typical ground of ore into fine-sand to silt-size particles, in order to improve beneficiation (Blowes et al., 2004); (2) the pyrite oxidation and the following weathering processes affecting it, wich lead to a grain size decrease; (3) the presumed concentration of Fe-rich secondary minerals (ex., copiapite, jarosite) (Jambor et al., 2000) within the silt and clay fractions. The chemical data also point out on the significant enrichement of Mn, Zn, Cu, As and Co in the silt and clay fractions. This is in agreement with other studies (e.g., Acosta et al., 2011), demonstrating that the fine grain size has a control on distribution of these elements.

Table 3. Geochemical properties of the waste material from the tailings pond

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	Mn	Cr	Co	Cu	Zn	Cd	Pb	As
	%							ppm							
Bulk Samples n=57															
Min.	20.56	2.66	5.18	0.05	0.00	0.41	0.24	71	11	12	101	53	0.14	219	61
Max.	69.01	17.03	21.31	3.5	1.11	2.35	3.53	588	104	60	2198	4026	9	7550	586
Mean	50.3	8.86	11.78	1.4	0.11	0.98	1.85	162	38	30	710	900	2	1555	195
SD	10.43	3.26	3.53	0.87	0.22	0.44	0.73	92	18	11	487	798	1	1582	119
Coarse and medium sand fraction (> 0.25 mm) n=9															
Min.	32.06	4.00	2.62	0.23	0.00	0.62	0.64	54	17	6	76	53	0.12	276	76
Max.	88.68	16.2	18.46	3.13	0.47	1.72	2.95	126	39	52	1154	875	2	3906	343
Mean	63.7	9.3	8.95	1.45	0.11	1.03	1.90	86	25	23	621	426	1	1725	193
SD	18.55	3.74	4.86	0.96	0.16	0.36	0.68	19	6	13	369	316	0.7	1363	83
Fine and very fine sand fraction (0,063 - 0,25 mm) n=10															
Min.	18.73	2.5	5.87	0.01	0.00	0.45	0.18	88	19	13.3	115	72	0.17	200	67
Max.	69.98	16.52	21.71	3.21	0.55	1.74	3.24	276	118	63	1188	1185	2	3518	346
Mean	49.7	9.96	12.15	1.72	0.09	1.16	1.96	149	49	31	579	564	1	1267	178
SD	16.92	4.95	5.24	1.09	0.17	0.43	1.08	67	28	16	317	385	0.94	1232	91
Silt and clay fraction (<0,063 mm) n=11															
Min.	20.98	2.76	13.05	0.04	0.00	0.47	0.24	92	11	32	204	73	0,15	267	67
Max.	55.13	11.68	21.08	2.99	0.39	1.59	3.03	320	110	61	1734	1946	4	3414	693
Mean	42.8	8.49	16.01	1.36	0.07	0.93	1.6	152	46	42	721	839	1	1209	227
SD	10.91	3.71	2.51	0.81	0.13	0.28	0.94	70	35	8	426	563	1	813	178

SD=standard deviation

The highest concentrations in silt and clay fractions is due to the high potential of the fine size grains for water retention and capillary forces that lead to an upwards enrichment of mentioned elements, in the form of water-soluble phases (Dold & Fontboté, 2001). In addition, elements such as Cu and Zn can be incorporated within the interlayers of the clay minerals (Dold & Fontboté, 2001). Contrary to the other elements, Pb has the highest concentration in the fraction similar to coarse and medium sand and diminishes with the decrease of the particle size. The higher concentration of Pb in the coarser size grain is due to low solubility of its (Conesa et al., 2008).

4.3.2. Multivariate statistics

The relationships between the parameters of the waste under study were examined with help of the Pearson correlation matrix (Table 4). The correlation matrix shows a very strong positive correlation between Al, K and Mg and a relatively high positive correlation of these elements with Na and Mn. The very good positive correlation can be explained by their association within the primary minerals of the waste (e.g., Al:K sericite; Al:Mg chlorite); in addition, these elements can be incorporated together in the structure lattice of the secondary minerals as Jambor et al., (2000) stated. Also, the studies carried out by Hammarstroma et al., (2005) pointed out that within jarosite, large amounts of Na as well as minor elements (Cu, Pb, As) can be incorporated.

Moreover, Al, K and Mg show also a relatively high correlation with Pb and As. Considering the mineralogy, this is likely because Pb is mainly co-precipitated with the jarosite group minerals (Dold & Fontboté, 2001), while As can substitute SO$_4$ within jarosite and gypsum minerals (Foster et al., 1998; Savage et al., 2000; Walker et al., 2009). Additionally, the XRD data confirmed the presence of secondary Pb-bearing minerals (plumbojarosite). Likewise, Cu, Zn and Cd, display a relatively high positive correlation with Na and Mg, whereas the positive correlation with Al, K and Mn is weak and not significant statistically. The correlations of minor elements with major elements may as well be assigned to the ability of secondary minerals to absorb minor elements (Hudson-Edwards et al., 1999; Kossoff et al., 2014).

The Pearson correlation matrix expresses a very strong relation between Fe - Co and Zn - Cd with very high positive values (0.99 for both pairs). The strong degree of correlation of the first pair is due to the presence of Co as minor element in pyrite, while for the second pair the explanation may be the well-known affinity of Cd for the Zn-bearing minerals, in this case sphalerite. Besides this, other significant relations were identified between Cu and Pb; Zn and Cd also display relatively high values of the correlation coefficient (0.71 Cu–Pb and 0.79 Cu–Zn, Cd respectively). These relationships suggest that Cu can be present in the metallic minerals (galena, sphalerite) as minor element.

The tailings pond typically consists of a both geochemically and physically heterogeneous material (Lottermoser, 2003); for this reason, the hierarchical

cluster analysis (HCA) was performed in order to identify the possible different types of waste. The results regarding HCA for all samples are reported in the form of a dendrogram (Fig. 4), where both physical and geochemical data were considered. Four main groups of samples have resulted from the HCA, which were numbered from I to IV (Fig. 4). To quantify the difference between clusters and summarize the characteristics of samples in different clusters, the average of all physico-chemical parameters for each main group is shown in Table 5. First of all, HCA reveals a clear separation between the samples collected from the beach of the tailings pond, dam and salt crusts. Thus, the first group (GI) consists of samples collected from the upper areas of the tailings pond beach and summarizes the largest number of samples. The second group (GII) comprises the salt crusts and holds two waste samples. The third group (GIII) is represented by samples from the upper levels of dam; to these, one sample from the horizontal surface of the impoundment, located close to the dam, is added. Finally, the last group (GIV) includes samples from lower part of the dam.
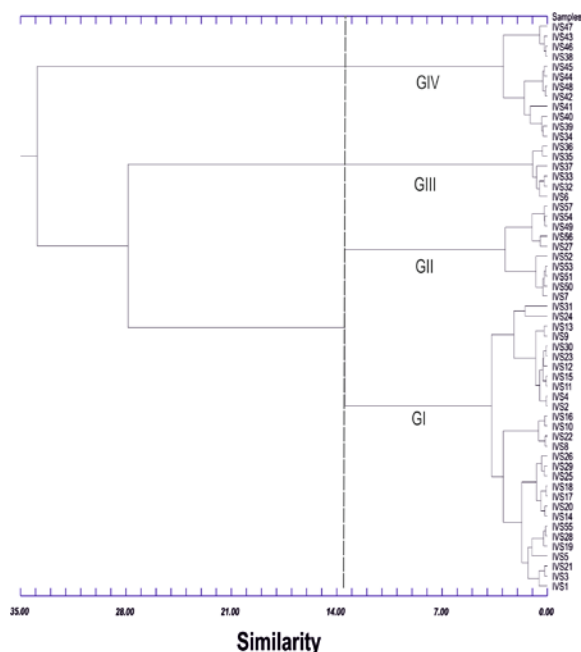

Figure 4. Cluster analysis by Ward linkage method and Euclidean distance

The highest concentrations of major and minor elements, as well as water-soluble fraction were identified in samples that consists GII (Table 1). This is in agreement with the mineralogical data, which show that salt crusts samples of GII display the largest amount of secondary minerals. Statistical results show that also the samples of GI have relative high amounts of major and minor elements as well as water-soluble fraction, but slightly lower than GII (Table 5). The samples from the dam surface (GIII and GIV) have

significant lower concentrations of minor elements compared with the samples from the beach of the tailings pond (GI and GII); GIII and GIV samples are also depleted in water-soluble fraction and silt and clay fractions (Table 5). This suggests that the concentration of minor elements is controlled either by the water-soluble fraction or the silt and clay fractions.

The geochemical data on each of the grain-size fraction confirm this by the highest concentrations of some elements (Fe, Mn, Zn, Cu, As, Co) identified within the silt and clay fractions (Table 3). In comparison with the other groups, the samples of the group GIII contain lowest concentrations in all major elements (e.g., Al, Mg, Ca, K) and some of the minor elements (e.g., Zn, Cd, Pb); on the contrary, Fe and Co amounts, as well as the quantity of fine and very fine sand-size waste grains, are high. Consequently, the highest concentrations of Fe and Co, likely due to the higher amount of pyrite within waste, seem to indicate the accumulation of the latter mineral within the fine and very fine sand-size fraction.

In terms of acidity, the samples that form GII are very acidic (pH – 2.65), while GIII samples, which have lower concentrations of Fe, show higher values of pH (3.15) (Table 5). This fact denotes the role of pyrite in the process of acidity production on the surface of the tailings pond from Straja Valley.

Principal Component Analysis (PCA) was performed on the basis of 18 geochemical variables, in order to identify the factors that are responsible for the accumulation of major elements and minor elements on the surface of the tailings pond. The results of PCA for all 57 samples are presented in Table 6 and figure 5. Three major principle components were identified, which explains 76.10 % of variance of the original data structure (Table 6): PC 1 (33.50%), PC 2 (29.97%) and PC 3 (13.63%).

PC 1 is related significant to some major elements (Al, Mg and Na), minor elements (Cu, Zn and Cd) and water-soluble fraction (Table 6). These elements can coexist within different secondary minerals resulting from the primary minerals weathering (Jambor et al., 2000). Therefore, the association of PC 1 with these elements suggests that the content of both major and minor elements on the surface of the tailings pond is influenced by the development of the secondary minerals. This statement is supported by the following considerations: 1) mineralogical data, which show that the content of secondary minerals within salt crusts is considerable; 2) geochemical data, suggesting that the highest concentrations of major and minor elements are in the crust samples, gathered within the GII cluster (Table 5); 3) positive correlations between the elements related to PC1, expressed by the correlation matrix (Table 4).

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Table 4. Pearson correlation coefficient

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	Cr	Mn	Co	Cu	Zn	Cd	Pb	As	pH	FS
SiO$_2$	**1**																
Al$_2$O$_3$	0.21	**1**															
Fe$_2$O$_3$	**-0.94**	**-0.3**	**1**														
MgO	0.04	**0.9**	-0.12	**1**													
CaO	-0.02	0.22	-0.14	0.25	**1**												
Na$_2$O	-0.16	**0.63**	0.19	**0.77**	0.03	**1**											
K$_2$O	**0.43**	**0.93**	**-0.56**	**0.81**	**0.27**	**0.45**	**1**										
Cr	-0.14	-0.18	0.08	-0.14	-0.09	-0.18	-0.14	**1**									
Mn	0.06	**0.31**	-0.18	**0.42**	**0.41**	**0.27**	**0.38**	-0.04	**1**								
Co	**-0.92**	**-0.38**	**0.99**	-0.2	-0.19	0.11	**-0.62**	0.08	-0.22	**1**							
Cu	**-0.39**	**0.46**	**0.34**	**0.57**	0.22	**0.65**	**0.27**	-0.07	**0.34**	0.27	**1**						
Zn	-0.21	**0.44**	0.18	**0.62**	0.1	**0.75**	**0.28**	-0.04	**0.47**	0.11	**0.79**	**1**					
Cd	-0.22	**0.43**	0.2	**0.6**	0.06	**0.75**	**0.27**	-0.05	**0.42**	0.13	**0.79**	**0.99**	**1**				
Pb	-0.19	**0.74**	0.06	**0.7**	**0.27**	**0.57**	**0.65**	-0.2	0.21	-0.01	**0.72**	**0.49**	**0.47**	**1**			
As	-0.05	**0.63**	-0.1	**0.6**	**0.43**	**0.28**	**0.66**	-0.16	**0.5**	-0.17	**0.41**	0.2	0.15	**0.68**	**1**		
pH	**0.41**	0.17	**-0.45**	0.16	0.09	-0.06	**0.29**	0.12	**0.42**	**-0.45**	-0.21	-0.09	-0.12	-0.11	0.22	**1**	
FS	**-0.28**	**0.5**	0.22	**0.55**	0.23	**0.47**	**0.37**	-0.16	0.08	0.15	**0.39**	**0.34**	**0.33**	**0.49**	**0.32**	**-0.36**	**1**

FS=soluble fraction, in bold, significant values at the level of significance alpha=0.05

Table 5. Cluster centroids of the tailings (mean values)

Group	N	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	Cr	Mn	Co	Cu	Zn	Cd	Pb	As	pH	FS	FC	FFF	FSC
		(wt %)							ppm								-	(wt %)			
GI	29	51.9	8.41	12	1.26	0.04	1.03	1.69	39	104	31	738	1018	2.64	1258	125	2.69	9.43	16	57.8	22.7
GII	10	44.5	13.3	12.6	2.74	0.28	1.52	2.72	32	243	31	1393	1862	4.44	4173	362	2.81	17	32.7	26.5	24.1
GIII	6	29	3.55	18.8	0.17	0.02	0.53	0.47	47	100	53	429	108	0.35	314	133	2.65	6.25	10.9	72.2	13.6
GIV	12	62.5	8.49	7.17	1.1	0.19	0.58	2.15	35	218	17	160	142	0.29	471	240	3.15	5.65	42.8	47.3	6.15

N=number of samples; FS=soluble fraction; FC=coarse sand size (1-0.25mm); FFF=fine and very fine sand size (0.25-0.063mm); FSC=silt and clay size (<0.063mm)

Table 6. Varimax-rotated factor matrix for Straja Valley tailings pond.

	PC1	PC2	PC3
SiO$_2$	0.02	**0.86**	0.04
Al$_2$O$_3$	**0.58**	0.22	0.14
Fe$_2$O$_3$	0.02	**0.92**	0.00
MgO	**0.61**	0.22	0.05
CaO	0.00	0.04	**0.61**
Na$_2$O	**0.75**	0.02	0.01
K$_2$O	0.40	**0.45**	0.10
Cr	0.00	0.01	0.00
Mn	0.00	0.01	**0.34**
Co	0.01	**0.93**	0.02
Cu	**0.57**	0.30	0.00
Zn	**0.84**	0.01	0.03
Cd	**0.80**	0.06	0.06
Pb	**0.74**	0.01	0.09
As	0.06	0.01	**0.75**
pH	0.04	**0.34**	0.08
FS	**0.36**	0.18	0.03
Variability (%)	32.50	29.97	13.63
Cumulative (%)	32.50	62.47	76.10

Moreover, all samples of GII as well as water-soluble fraction are high associated with the positive values of PC 1 (Fig. 5B, D). PC 2, which accounts for 29.97% of the total variance (Table 6), seems to be related to Fe, Co and P (Figure 5A). According to HCA (Table 5 and Fig. 4), the samples of GIII have the highest concentration in Fe and Co and they are associated with the positive PC2 (Figure 5B, D). On the contrary, the GIV samples display the lowest concentration of the discussed elements (Table 5), showing their opposite position in respect of GIII samples (Figure 5B, D). Therefore, high positive association of Fe and Co with PC 2 (Fig. 5A) and the absence of other major elements loading (e.g., Al, K, Mg) indicate that pyrite is responsible for the accumulation of these elements and its abundance is the second principal component. PC 3 which accounts for 13.63 % of the total variance in the tailings pond shows high loadings for Ca and As, while that of Mn is slight (Table 6 and Fig. 5C), indicating a common behavior. This may suggest that PC 3 expresses the amount of Ca-bearing minerals. Moreover, the concentration of the Ca-bearing minerals seem to have a control on As and Mn distribution. These findings are supported by the high positive association of the GII and GIV with PC 3 (Table 6 and Fig. 5D). The GII and GIV have the largest concentrations of Ca, Mn and As, in contrast with the GI and GIII (Table. 5). Chemical analyses revealed that Mn and As are highly concentrated in silt and clay fractions.

The highest concentration of Mn and As in GII revealed that their abundance is equally controlled by water soluble fractions and silt and clay fractions

(Table 5). Nevertheless, the concentrations of Mn and As also exceed in the GIV samples, where the water soluble fraction and silt and clay fractions occur in small quantities (Table 5). According to Dold & Fontboté, (2001), Mn is very mobile in acidic environments, but when pH of the solutions increases, Mn hydrolyses as Mn(OH)$_2$. Studies conducted by Jurjovec et al., (2002) have shown that the dissolutions of aluminosilicates and carbonates are involved in the neutralization of the acidic solutions. The dissolution of the Ca-bearing carbonates, as well as the aluminosilicates dissolution (e.g., plagioclase feldspars) realease Ca^{2+} in acid mine water, so as the gypsum can precipitate (Lindsay et al., 2015; Moncur et al., 2005). Consequently, the presence of gypsum explains the As distribution, because this element can be incorporated in the gypsum lattice, as noted earlier (Foster et al., 1998; Savage et al., 2000; Walker et al., 2009). Moreover, As dissolved in AMD can co-precipitate and sorbed on solid phase (e.g. secondary minerals) as the pH increases (Frau et al., 2010). Therefore, considering the quoted previous studies, it can be presumed that the accumulation of Mn and As are controlled by the acidity of the solutions. In addition, As is controlled by the precipitation of gypsum as well. This hypothesis is sustained by the pH values of the GIV (average pH = 3.15), which are higher than that of the other groups (Table 5). In conclusion, in the areas where the acidity of solutions decreases due to the neutralization potential, the concentration of Mn and As may occur.

4.3.3. Geochemical mapping and identification of the environmental risk

The maps showing the distributions of major and minor elements and water-soluble fractions were drawn to identify their areas of concentration on the surface of the tailings pond (Fig. 6). The distribution of the water-soluble fraction shows that it increases in the flat areas of the waste beach and where the crust samples were observed. The geochemical distribution of some of the major elements (e.g., Al, Mg, K) and minor elements (e.g., Pb, Cu, As, and Zn partially) display a very similar pattern.

According to the HCA, these perimeters consist of GII samples, which are also defined by higher amounts of silt and clay fraction, relative to other groups. These samples were collected nearby the water-pool (Fig. 1) and from the northern sectors of the tailings pond. This supports the hypothesis that the water-soluble fraction controls the accumulations of both major and minor elements on the surface of the tailings pond, as PCA suggested. In addition, it seems like the topography of the pond surface also played a role in the accumulation of most of the chemical

elements across the surface of the waste deposit.

This may be explained by the following sequence of events: (1) during dry periods, the secondary minerals form by the evaporation of pore-waters within the detritus, on the slightly elevated surfaces of the beach; (2) during rainfall, the secondary minerals are dissolved by water and transported towards the lower parts of the tailings pond; (3) the leachates enriched in major and minor elements accumulate in the lower sectors of the tailings pond and, during the dry periods, another sequence of secondary minerals appears, through evaporation and precipitation (Dold & Fontboté, 2001; Bea et al., 2010). In terms of the environmental risk, during dry seasons the very fine particles that concentrate significant amounts of minor elements can be transported by strong winds towards the surrounding areas. Moreover, the evaporative layer of secondary phases which is formed during dry periods can be dissolved by heavy rainfall, so as considerable amounts of major and minor elements can be leached and transported towards the neighboring areas.

The geochemical maps also show that the highest concentrations of Fe and Co were found in samples collected from the upper level of the dam (Fig. 6), where the major elements and minor elements has the lowest concentrations. The mineralogical data revealed that the samples of the upper level of the dam consist mainly of pyrite, which controls the Fe distribution, as demonstrated by the mineralogy, PCA and HCA. As emphasized previously, the samples from the upper level of the dam cluster within GIII group and are extremely acidic (average pH = 2.65). Consequently, the lowest contents of major and minor elements in this area can be explained as follows: under highly acidic conditions, silicate dissolution rate increases (Jambor et al., 2002; Jurjovec et al., 2002; Salmon & Malmström, 2006), leading to the attenuation of the major elements (e.g., K, Al, Mg); the metals (e.g., Pb, Zn, Cu, As, Cd) exhibit high dissolved concentrations and a larger mobility in acidic conditions as well (Lindsay et al., 2015). Likewise, on the lower part of the dam (cluster GIV), the concentration of minor elements is very low.
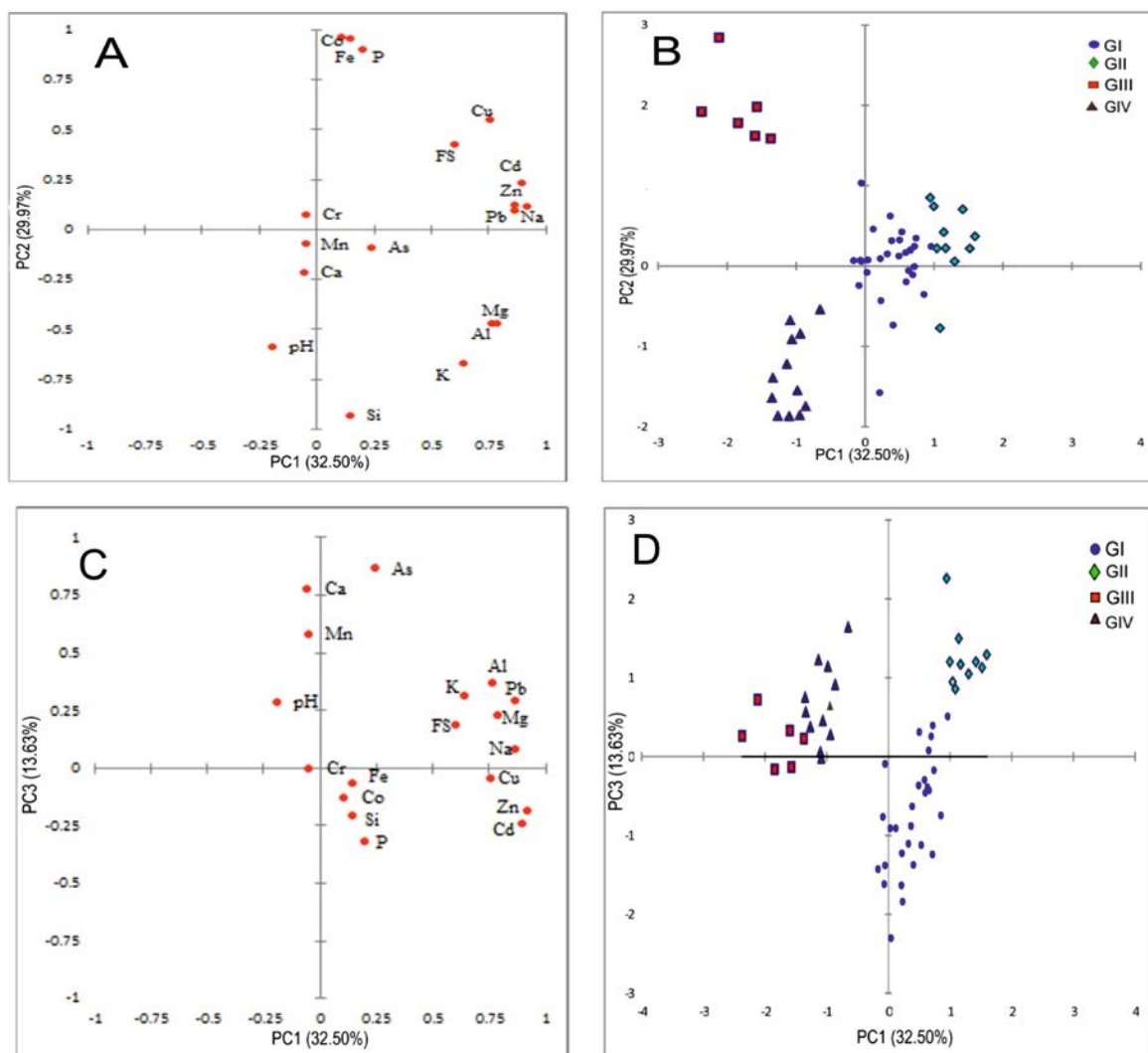

Figure 5. Projection of the variables (A, C) and the samples (B, D) of the PC

Soluble
Fraction (%)
- 1.48-6.04
- 6.05-8.91
- 8.92-11.65
- 11.66-13.99
- 14.00-16.47
- 16.28-20.50
- 20.51-26.76
- 26.77-34.70

Al (%)
- 2.66-5.25
- 5.26-7.11
- 7.12-8.46
- 8.47-9.70
- 9.71-11.00
- 11.01-12.41
- 12.42-14.32
- 14.33-17.03

Mg (%)
- 0.05-0.51
- 0.52-0.90
- 0.91-1.27
- 1.28-1.63
- 1.64-1.96
- 1.97-2.35
- 2.36-2.85
- 2.86-3.50

K (%)
- 0.24-0.88
- 0.89-1.31
- 1.32-1.59
- 1.60-1.88
- 1.89-2.12
- 2.13-2.41
- 2.42-2.82
- 2.83-3.53

Mn (%)
- 71.00-103.44
- 103.45-11.55
- 111.56-116.63
- 117.64-129.80
- 129.81-143.99
- 144.00-212.92
- 212.93-289.96
- 289.97-587.89

Fe (%)
- 5.18-7.84
- 7.85-9.61
- 9.62-11.19
- 11.20-12.33
- 12.34-13.59
- 13.60-15.74
- 15.75-18.59
- 18.60-21.31

Pb (ppm)
- 219-938
- 939-1685
- 1686-2433
- 2434-3238
- 3239-4158
- 4159-5250
- 5251-6400
- 6401-7550

As (ppm)
- 61-120
- 121-160
- 161-210
- 211-250
- 251-310
- 311-370
- 371-470
- 471-590

Cu (ppm)
- 101-364
- 365-585
- 586-742
- 743-922
- 923-1120
- 1121-1334
- 1335-1683
- 1639-2197

Zn (ppm)
- 53-193
- 194-754
- 755-894
- 895-988
- 989-1100
- 1101-1240
- 1241-1970
- 1971-4030

Co (ppm)
- 12-19
- 20-24
- 25-29
- 30-32
- 33-36
- 37-43
- 33-51
- 52-60

Legend

Dam

Water pool

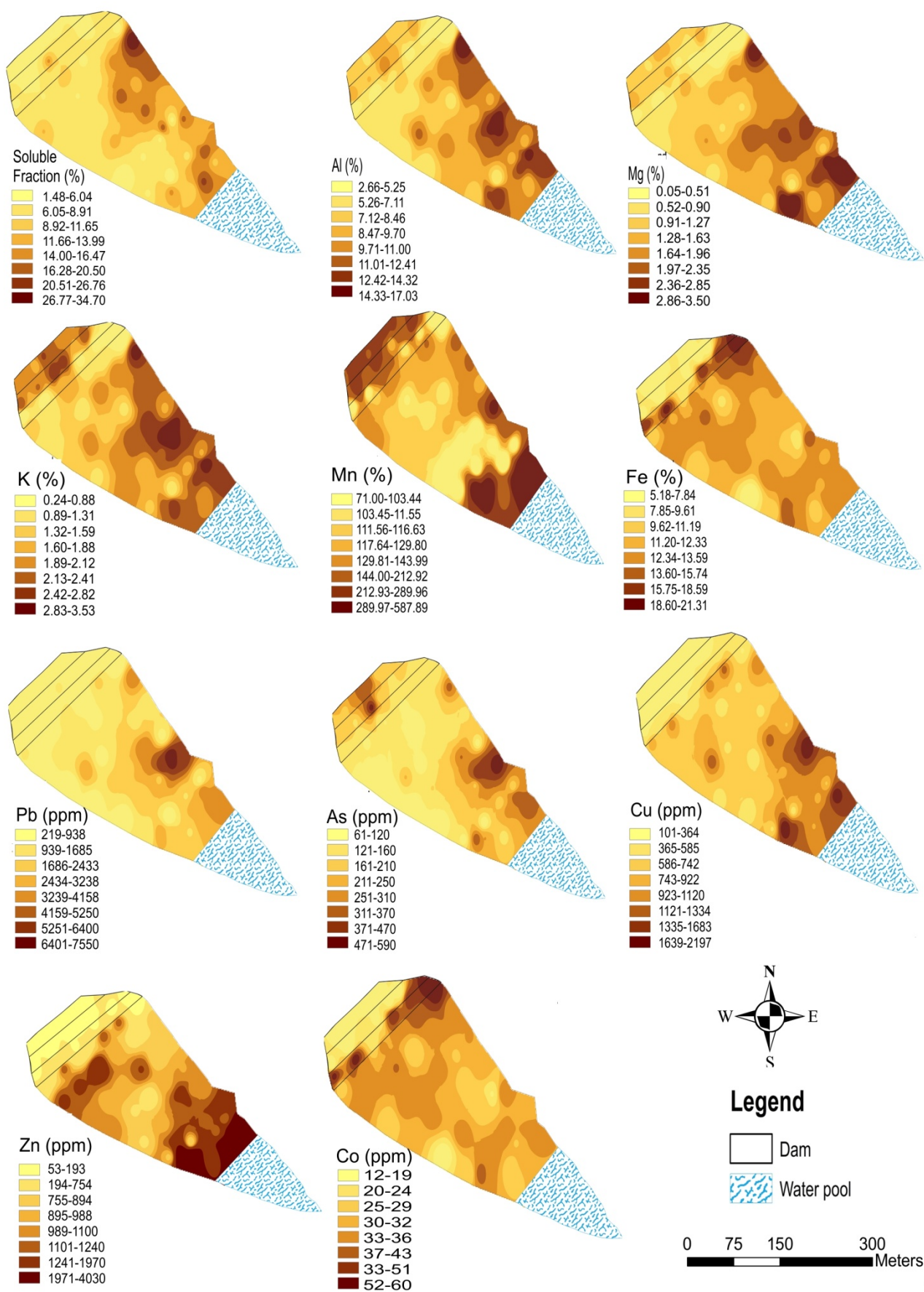0   75   150   300
                        Meters

Figure 6. Geochemical distributions of the water-soluble fraction, major and minor elements on the surface of tailings pond.

The minor elements depletion is due to low abundance of water soluble fraction and clay and silt fractions, which usually concentrate considerable amounts of such elements. These aspects could be explained by the appearance of the dam, which shows that it was subjected to high runoff erosion, during which the fine and very fine material as well as water soluble fractions were washed away. These highly acidic waters along with the dissolved constituents of the tailings pond present a real risk to the surrounding environment.

5. CONCLUSIONS

This study focused on the physical, mineralogical and geochemical descriptions of the waste from the flanks and the upper surface of the tailings pond of Straja Valley. The mineralogical data reveal that the most abundant primary minerals are quartz, sericite and pyrite. The secondary minerals were found especially within the salt crusts samples, consisting of K-jarosite, alunite, hydroniumjarosit, plumbojarosite, gypsum and subordinate copiapite. Also, in the crust samples, clay minerals (usually kaolinite and rarely illite) were identified. The geochemical analyses revealed very high concentrations of Pb, Cu, Zn and As, while Cr, Co and Cd show a moderate abundance. The highest amounts of major and minor elements (e.g., Fe, Mn, Zn, Cu, As) were measured in silt and clay fractions. These fractions appear in a relatively high percentage, i.e., around 22% of the waste mass. The waste of the tailings pond exibits very high acidity (average pH = 2.81). The multivariate statistics and geochemical maps reveal that the most of major and minor elements are controlled by the formation of secondary minerals. The degrees of accumulations of the secondary minerals are conditioned by climate and surface topography.

The multivariate statistics separated four groups of waste and identified three principal components that contribute to the distribution of all elements across the surface of the pond tailings. Principal components that lead to the accumulations of major and minor elements on the surface of the tailings pond are: 1) water-soluble fraction (the formation of secondary minerals phases); 2) Pyrite; 3) Ca-bearing minerals that are responsible for Ca, Mn and As distribution.

The study has also drawn attention on the pollution risk. Therefore, the detailed description of the physico-chemical and mineralogical parameters suggest that all material of the tailings pond represent a high risk of environmental pollution. However, from those four types of waste identified, the highest risk is associated to GII tailings, due to their highest

concentrations in water soluble fractions, major and minor elements, silt and clay fractions as well. This group, on the one hand, can carry out considerable quantities of minor elements during rainfall in wet seasons. On the other hand, the fine and very fine waste particles, rich in minor elements, can be transported by wind, during the dry seasons. The GI waste as well has very high concentrations of minor elements, being very susceptible to transport towards the environment. By its position in the in higher areas of the tailings pond beach, GI waste may be a source of both major and minor elements, for the GII tailings. For this reason, GI waste may be considered to present a higher environmental risk than GII. Despite their lower concentrations of minor elements the GIII and GIV types of waste, which consists of tailings from the dam, present a risk for the environment for two reasons: (1) due to its high acidity, the GIII waste increases the mobility of minor elements; (2) due to the morphology of the waste deposit, the GIV tailings are more susceptible to erosion and transport towards the surrounding areas.

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