WASTE OF THE STRAJA VALLEY TAILINGS POND (SUCEAVA COUNTY, ROMANIA). GEOCHEMICAL PROPERTIES AND ENVIRONMENTAL RISKS RELATED TO WIND-DRIVEN REMOVAL

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Abstract: The tailings of Straja Valley waste deposit consist mainly of minerals resulting from the metallic ores and their host schist of Lesu Ursului mining field (primary minerals). Additionally, secondary minerals produced through the weathering of the first ones were identified (Na- and Pb-jarosite, Mg-copiapite, gypsum, alunite, apjohnite, and goethite). Two grain-size classes were separated namely coarse grains (CG) (size larger than 0.25 mm) and fine grains (FG). The descriptive statistic data showed that the geochemical properties of the waste depend on its location on the tailings pond, abundance of the soluble fraction (in close relation with secondary hydrated sulfates) and, to a lesser extent, the waste grain size. Principal Component Analysis (PCA) carried out on geochemical data revealed the following patterns of waste: (i) pyrite-rich tailings from the waste beach are frequently fine-grained and have a higher Cu content; (ii) while the coarse-grained waste is rich in silicates, it also contains secondary minerals that trap Pb (Na-jarosite, Pb-jarosite, gypsum); (iii) if the silicate-rich tailings are controlled by quartz, they are coarse-grained and depleted in secondary minerals; (iv) the fine-grained silicate-rich waste also contains secondary minerals (e.g., Na-jarosite, Mg-copiapite, gypsum, alunite, and clay minerals) that collect Pb, Al, Mg, Ca, and Na in their structure. The environmental risks related to wind-driven transport of waste during long drought periods can be presumed as following: (i) mechanical pollution with quartz and chemical pollution with Pb, Zn, Cd trapped in sphalerite ± galena, Pb-jarosite, Mg-copiapite, goethite, apjohnite, and clay minerals, when wind exceeds 7.3 m/s; (ii) pollution with fine-grained pyrite (and Cu, Zn, Cd within) or secondary minerals that accumulate Pb and As (Pb-jarosite, Mg-copiapite, apjohnite, and goethite), when the wind speed is less than 7.9 m/s.

Keywords: tailings, grain size, secondary minerals, geochemistry, PCA, airborne removal.

1. INTRODUCTION

The technological activities of mining and related ore-processing generate large amounts of waste, most of which bearing variable amounts of sulfides. Among these waste deposits, the unconfined tailings ponds seem to be the most susceptible to act as a potential source of environmental pollution. The increased environmental risk is in connection with the texture of the waste, namely the grain size. The texture of tailings looks similar to that of sands, silts, and clay fraction, as they are described in the field of sedimentary petrology. As a result, waste grains have a large specific surface area, which makes them more sensitive to weathering agents (Pennell, 2016).

Another consequence of the tailings' size is their high susceptibility of being removed from the surface of the waste deposit. This may occur through mechanisms such as wind-driven transport of fine particles during drought periods (McKenna-Neuman et al., 2009; Khademi et al., 2018; Trifi et al., 2019) and mechanical transport of tailings grains by the surface runoff during heavy rains (Stumbea, 2013) or dam failure (Kossoff et al., 2014).

The presence of sulfides (especially pyrite) in the mine waste is a widely accepted factor that can initiate polluting processes. When the sulfide grains are small, as in the tailings ponds, the weathering is more intense and the environmental risk increases. The triggering process is that of fine-grained sulfide oxidation. The oxidation process unfolding under

wet conditions results in the generation of acidic leachates (acid mine drainage – AMD) (Jackson & Parbhakar-Fox, 2016; Ceniceros-Gómez et al., 2018), usually rich in sulfates and potentially toxic elements. These solutions may accumulate either within the pore of the waste (pore-water) or as puddles on the beach of the tailings pond. The heavy rains may produce significant AMD that flows toward the surrounding areas, charged with potentially toxic elements (Bauerek et al., 2013; Zheng et al., 2019). During dry periods, the water evaporates from the pore-leachates or leachate puddles, resulting in precipitation of secondary minerals (mostly hydrated sulfates) that accumulate toxic elements in their structure (Hiller et al., 2013; Smuda et al., 2014; Root et al., 2015; Courtin-Nomade et al., 2016).

The tailings ponds resulted from the metal-extraction activities in the Polymetallic Belt of Eastern Carpathians (Romania) were intensely studied during the last decade, in terms of mineralogy and geochemical properties (e.g., Stumbea, 2013; Chicoș et al., 2016; Paiu et al., 2017). However, the risks of wind-driven removal and transport of tailings towards the surrounding areas were less approached. Therefore, the following objectives have been set for the present study: (i) to identify the factors/processes that control the mineralogical and geochemical properties of the waste in the tailings pond; (ii) to identify whether the mineralogy and geochemistry of the waste is related to the tailings grain size; (iii) to determine if the waste is susceptible to airborne removal from the tailings pond and which are the associated environmental risks.

2. GEOLOGY AND STUDY AREA

2.1. Geology

The tailings pond in Straja Valley has stored the waste resulted from the ore-processing plant of Tarnița that was extracting metals from the sulfide mineralizations of the Leșu Ursului metallogenic field. Along with the metallogenic field of Fundu Moldovei, located about 35 km to the north-west, the Leșu Ursului metallogenic field is a subdivision of the Fundu Moldovei–Leșu Ursului metallogenic district. This district has a central position in the Polymetallic Metallogenic Belt of the Eastern Carpathians (Fig. 1), which also includes the northern metallogenic district of Borșa–Vișeu and the southern district of Bălan–Fagu Cetății (Berbeleac, 1988). The polymetallic belt is oriented NW-SE and ranges over 160 km.
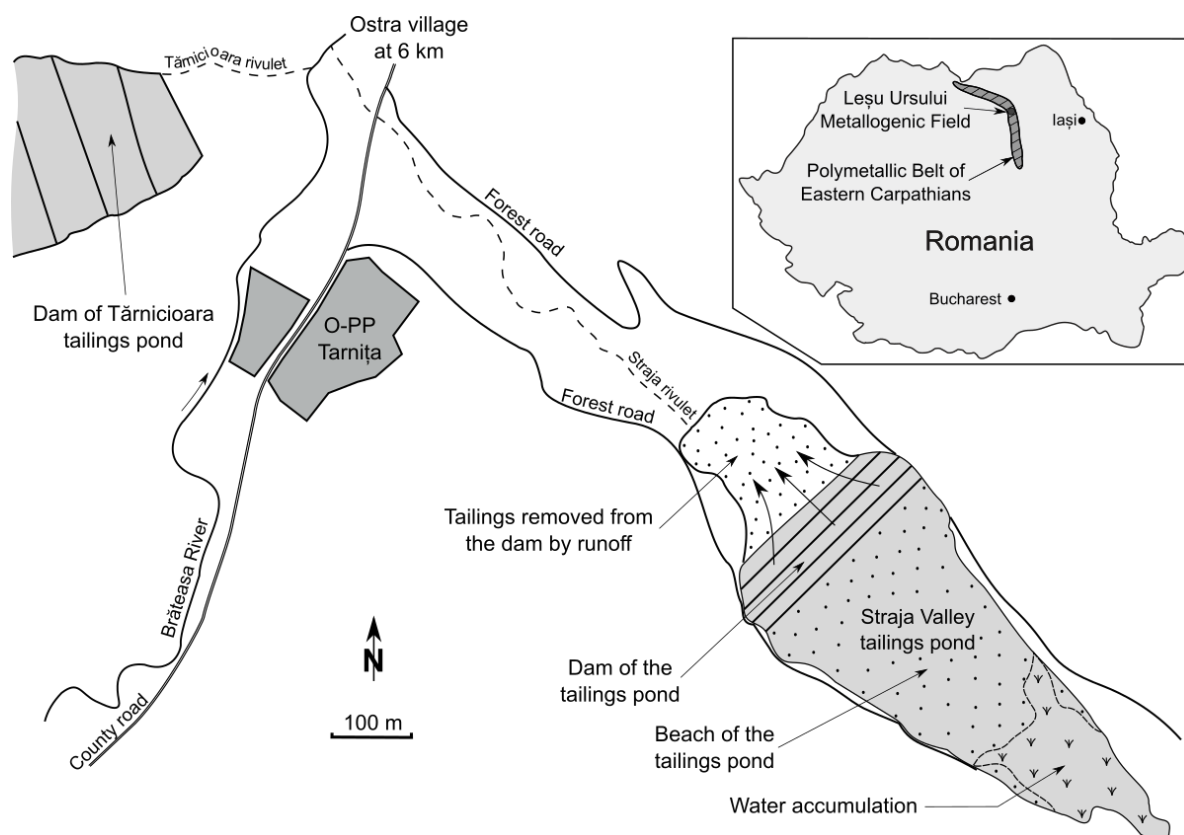

Figure 1. Sketch of the Straja Valley tailings pond and surrounding areas. Location of the Polymetallic Belt of Eastern Carpathians on the territory of Romania. O-PP – Ore-Processing Plant.

Like all metallogenic fields in the Polymetallic Belt of Eastern Carpathians, the ores of the Leşu Ursului metallogenic field are hosted by the low-grade metamorphic rocks of the Group of Tulgheş. This group is of Cambrian age (Iliescu et al., 1983) and consists of schists with variable proportions of quartz, micas (muscovite, paragonite), chlorite, albite, and biotite. The most common types of rocks are quartz-sericite-chlorite schist, quartz-chlorite schist, and quartz-sericite schist (Berbeleac 1988).

The ore deposits in the Polymetallic Belt of Eastern Carpathians are of volcano-sedimentary origin, consist in sulfides, and display a large abundance of Cu-rich pyrite. In the Leşu Ursului metallogenic field, the polymetallic ore appears as a massive stratiform body that shows gradual transitions to a well-developed disseminated zone (Kräutner, 1984). Pyrite (usually Cu-rich), chalcopyrite, sphalerite, and galena control the ore mineralogy; as accessory minerals, marcasite, arsenopyrite, bournonite, tetrahedrite, magnetite, and covellite were identified (Chicoș et al., 2016). The minerals of ore-hosting rocks appear as gangue minerals.

2.2. Location and description of the waste deposit

The study waste deposit is one of the five tailings ponds of the area that collected the slurry of the Tarnița metal-extraction facility. The processing of ore started in 1967, at the same time as the mining activity at Leşu Ursului, but the tailings pond of Straja Valley became operational in 1973. In the mid-2000s, the activity ceased in the mining perimeter.

The tailings pond is located at about 1 km upstream the confluence of Straja rivulet with Brăteasa river. The nearest inhabited area is the Ostra village, situated over 6 km to the north. The waste deposit is oriented NW-SE; it is a 500 m long and a maximum 250 m wide valley-type tailings pond. The dam is 28 m high and confines about 2.3 M m^3 of currently dry waste. Towards the dam, the beach of the tailings pond ends with a 50 cm high ridge, which prevents the flow of runoff over the dam slope.

The waste deposit is situated at an altitude of 870 m, in a perimeter with a climate specific to mountain areas from the temperate climate regions. During the summer, the average temperature of the air is around 15°C, while the humidity is 80 %. The average speed of the wind is 3.8 m/s, blowing mostly from NW. The rainfall regime is in between 100 and 110 mm/year.

3. MATERIALS AND METHODS

3.1. Sampling

A total of 60 samples were collected from the surface of the tailings pond, considering that the superficial layers of waste are the most reactive to weathering agents. The sampling was carried out during autumn, it covered the surface of both beach and dam slopes of the waste deposit and followed a rectangular grid of 50 × 60 m on the beach and 50 × 30 m on the dam. The tailings were sampled with the help of a plastic paddle, stored in plastic bags and sealed until analyses.

3.2. Laboratory analyses

Based on the grain size, two classes of tailings were determined, namely the particles larger than 0.25 mm (named coarse-grains in the present study) and particles smaller than 0.25 mm (fine-grains). The size-limit of 0.25 mm was chosen due to the textural similitude of tailings, with sand and it separates the coarse and medium sands, from fine sand, silt and clayey fractions (Wentworth scale, in Chotiros, 2017). To determine the tailings abundance in the two classes, the dry sieving method was used. In this respect, the waste samples were passed through the 0.25 mm sieve and the resulting fractions were weighted; the weight percent were calculated afterward.

A preliminary estimation of the waste mineralogy was made using a Stereo Optika SZM2 stereomicroscope, with a magnification of up to 45×. Further, detailed identification of the mineral phases was performed with the help of a Philips PW 1739 X-ray diffractometer equipped with monochromatic CuKα (1=1.54056 Å), operating at the following parameters: 40 KV, beam current of 20 mA, 0.05° 2θ step-size with 2 s per step. The abundances of mineral phases were roughly evaluated by comparing the main peaks.

The density of waste was determined as follows: a fraction of waste was weight and placed within a graduated cylinder; next, water was poured in. The resulted slurry was left to decant for 30 minutes and the volume of the solid was read on the cylinder. Then, the ratio between waste weight and its volume was calculated.

To determine the waste pH and abundance of the soluble fraction, the single extraction leaching tests were carried out. For this purpose, 10 g of waste was mixed with 10 mL of distilled water, within a beaker. Then, the beaker was stirred at 150 rpm, for 1 hour, and the resulted slurry was passed

through a 0.2-μm cellulose filter. After drying it in an oven at 50°C, the insoluble fraction left on the cellulose filter was weight; next, the percentage of the soluble fraction was calculated. Using a Corning M555 pH/ion meter, the pH of the liquid collected during the slurry filtration was measured.

The chemical analyses of the tailings were carried out with an X-ray Fluorescence Spectrometer – EDXRF Epsylon 5. In this regard, the samples were ground previously to a grain size of less than 50 μm, then mixed with Hoechst wax and pressed to pellets. As reference materials to calibrate the spectrometer, river and lake sediments, but also soil samples were used.

3.3. Statistical analyses of data

The statistical processing of data was conducted using the XL Stat Pro 7.5 software. The univariate statistical methods were performed to evaluate the distribution of the geochemical variables. For this purpose, the central tendency (mean) and dispersion (range and coefficient of variation) were calculated. Also, to reduce the dimensions of datasets, the Principal Component Analysis (PCA) was performed. This approach helped to identify the factors that influenced the texture, mineralogy, and geochemistry of the waste. Before PCA, the data were log-transformed and standard scores were calculated so that the variables get equal weight, in the statistical population.

4. RESULTS AND DISCUSSIONS

4.1. Tailings description

The beach of the tailings pond has a light gray colour, due to the salts that precipitate from the pore-waters or puddles accumulated during rainfall. On the contrary, the waste of the dam is ochre, probably because of the frequent removal of secondary minerals by runoff, but also to more intense oxidation of pyrite. In some areas, the beach is whitish as a result of the airborne quartz accumulation.

The usually sandy texture of waste results from the technological process of ore crushing, during the metal extraction in the flotation plant. The grain-size analyses revealed that about 27 wt % of the beach waste has a texture similar to coarse and medium sand (tailings larger than 0.25 mm). The waste of the dam is characterized by a higher abundance of coarse tailings, i.e., around 40 wt %. The two particle-size distributions may account for the following processes: (i) the superficial waste

sampled from the beach consists mainly of smaller particles, which settle down the last, from the slurry of the active tailings pond; (ii) the waste of the dam is depleted in small particles, due to their higher susceptibility of being removed and transported by runoff during heavy rains.

4.2. Mineralogy of the waste

The dominant minerals in the studied waste originate from the host rocks of the sulfide ores (silicates) and the mineralizations themselves (sulfides) (Table 1). Among the primary silicates, quartz is the most abundant, followed by white-greenish micas (muscovite and paragonite), chlorite, rare albite, traces of biotite and, accidentally, garnet. The sulfides consist of pyrite and sphalerite, but XRD patterns of galena were also identified.

Table 1. Minerals identified by XRD

Mineral phases	Beach	Dam
Primary minerals		
Quartz	XX	X
Micas	XX	X
Chlorite	XX	X
Albite	X	(X)
Pyrite	X	XX
Sphalerite	X	XX
Galena	(X)	X
Secondary minerals		
Natrojarosite	X	-
Plumbojarosite	X	(X)
Magnesiocopiapite	X	(X)
Goethite	X	X
Gypsum	XX	X
Alunite	X	-
Apjohnite	X	X
Illite-Montmorillonite	XX	(X)
Kaolinite	X	-

(X) doubtful

Additionally, the XRD analyses revealed a second group of minerals, consisting of hydrated sulfates (Na- and Pb-jarosite, Mg-copiapite, gypsum, alunite, apjohnite) and goethite (Table 1). These minerals account for the weathering of primary minerals in the waste, through sequences of processes that include sulfide (especially pyrite) oxidation, dissolution, dilution, evaporation, and precipitation. Alpers et al., (1994) defined these minerals as secondary minerals. Since no clay mineral was reported in relation with either schist or associated mineralizations, it may assume that illite-montmorillonite and kaolinite are also secondary minerals.

4.3. Statistical approach of geochemical data

4.3.1. Descriptive statistics

The element concentrations in the waste, determined by XRF, are presented in Tables 2, 3, 4, and 5. The chemical properties of the tailings are closely related to the mineralogy of waste as follows: (i) Si, Al, Mg, Na, K, and part of Fe originate from the silicates of the schists (quartz, sericite/muscovite, and chlorite) and clay minerals (illite-montmorillonite and kaolinite); (ii) most of Fe, but also Co, Cu, Zn, Cd, Pb, and As, appear as either major elements in sulfides or minor elements in some primary and secondary minerals (oxyhydroxides and hydrated sulfates).

The statistical parameters in table 2 indicate specific geochemical patterns of the tailings samples, depending on their location on the surface of the waste deposit. Besides, the abundance of soluble fraction seems to be another factor that controls the distribution of elements over the surface of the tailings pond. The soluble fraction is much more abundant within the waste of the beach (Table 3) because it consists mostly of soluble secondary minerals (especially hydrated sulfates) (Table 1). The latter precipitate during the evaporation of water from the puddles formed on the surface of the beach.

In the course of subsequent rainfalls, the soluble salts are dissolved and produce acidic leachates (acid mine drainage – AMD) that remain on the surface of the beach. This sequence of processes, consisting of dissolution – evaporation – precipitation, can take place several times during summer. The hydrated sulfates resulting from the acidic leachates also explains the lower pH of the tailings on the beach of the waste deposit.

The samples collected from the beach of the tailings pond are more abundant in Si compared to those of the dam (Table 2). This aspect is in agreement with the field observations, which revealed 1-2 mm thick layers of quartz deposited by the wind in many areas of the beach. The lower Al and Mg contents and, to a lesser extent, Na and K in the waste of the dam may have the following meanings: (i) the phyllosilicates are more susceptible to be removed from the dam tailings by runoff, during rainfall; (ii) the secondary minerals rich in Al, Mg, Na, and K (natrojarosite, magnesiocopiapite, alunite, apjohnite, illite-montmorillonite, and kaolinite) are more abundant in the waste collected from the beach. Because of its higher specific gravity compared to silicates, pyrite of the dam waste is probably less mobile during runoff, leading to an iron-enrichment of the slope tailings.

Table 2. Major elements (wt%) in the waste, depending on the sampling point localization

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Beach ($n = 38$)							
Min.	36.45	5.06	10.12	0.85	0.00	0.89	0.88
Max.	56.71	17.29	17.54	2.97	0.66	1.65	3.47
Mean	47.33	11.16	12.92	1.77	0.07	1.27	2.02
C.V.	0.20	0.36	0.13	0.50	1.88	0.25	0.40
Dam ($n = 22$)							
Min.	19.34	3.44	4.79	0.09	0.00	0.39	0.11
Max.	64.09	9.27	22.55	2.94	0.19	1.22	2.93
Mean	39.26	6.03	17.05	1.11	0.07	0.77	1.23
C.V.	0.41	0.52	0.42	0.92	1.21	0.31	0.84

C.V. – coefficient of variation

Table 3. Potentially toxic elements (mg/kg), pH and soluble fraction (SF) (wt%) in the waste, depending on the sampling point localization

	Mn	Co	Cu	Zn	Cd	Pb	As	pH	SF
Beach ($n = 38$)									
Min.	104	23	423	543	1.46	475	102	2.44	7.35
Max.	161	43	1830	1849	4.42	3342	340	2.72	36.81
Mean	137	32	846	924	2.45	1682	175	2.55	15.08
C.V.	0.13	0.22	0.46	0.43	0.38	0.56	0.50	0.07	0.65
Dam ($n = 22$)									
Min.	98	12	122	68	0.16	189	142	2.34	4.61
Max.	340	60	1042	599	0.67	1162	736	3.97	9.75
Mean	203	40	468	239	0.36	502	296	3.05	6.92
C.V.	0.50	0.43	0.72	0.73	0.52	0.58	0.77	0.21	0.26

The sulfides of the waste (pyrite, frequently rich in Cu, sphalerite, galena) are in control of the potentially toxic elements Cu, Zn, Cd, and Pb. However, the larger content of the latter elements within the tailings collected from the beach (Table 3) may also be related to the capacity of some primary and secondary minerals to trap them as minor elements in their structure. Based on information from previous works, the mineral species in table 1 that may explain the higher contents of Cu, Zn, Cd, and Pb are: (i) pyrite, jarosite, goethite, gypsum and illite-montmorillonite, which may trap Cu (Ferreira da Silva et al., 2009; Sherriff et al., 2011; Chen et al., 2012; Hiller et al., 2013); (ii) jarosite, goethite and kaolinite that are known to collect Zn (Hammarstrom et al., 2005; Romero et al., 2007; Graupner et al., 2007; Ferreira da Silva et al., 2009; Smuda et al., 2014; Root et al., 2015); (iii) pyrite, sphalerite, jarosite, apjohnite, and kaolinite, which may control de Cd amount (Giudici et al., 2002; Moncur et al., 2005; Jamieson et al., 2005; Carmona et al., 2009; Ferreira da Silva et al., 2009); (iv) pyrite, magnesiocopiapite, jarosite, apjohnite, goethite and clay minerals that are reported to concentrate Pb (Graupner et al., 2007; Savage et al., 2008; Deditius et al., 2011; Hayes et al., 2012; Courtin-Nomade et al., 2016).

The geochemical properties of fine- and coarse-grained waste are broadly similar (Tables 4 and 5). However, some geochemical patterns were recorded: (i) silica shows a higher abundance in the coarse-grained waste, probably due to quartz, which frequently appears as large grains; (ii) the contents of Fe, Cu, and Zn are higher in the fine-grained tailings, which consist mostly of sulfides that underwent mass loss during the technological process of metal extraction.

4.3.2. Multivariate statistics

To reduce the number of dimensions and to bring out the strong patterns from the data population, the Principal Component Analysis (PCA) was performed. By using the Kaiser criterion (Kaiser, 1960), three principal components were determined, accounting for around 82 % of the total variance. The results are presented in figure 2 as PCA biplot diagrams.

The PC1 axis (Fig. 2a,b) seems to reflect the role of primary minerals in the geochemical distribution of the elements within the waste. Thus, the negative PC1 accounts for pyrite (often cupriferous), while the positive PC1 is influenced by the presence of silicate minerals (i.e., quartz, sericite/muscovite, chlorite), but also sphalerite and rare galena. Principal component PC2 (Fig. 2a) is related to the geometry of the tailings pond as follows: negative PC2 reflects the samples collected from the beach, whereas positive PC2 refers to the detritus from the dam of the waste deposit.

Table 4. Major elements (wt%) in the waste, depending on the grain size

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Coarse tailings (*n* = 30)							
Min.	16.21	2.07	6.63	0.02	0.11	0.56	0.09
Max.	68.01	14.99	22.45	2.71	0.49	1.90	2.88
Mean	48.32	10.52	11.37	1.85	0.17	1.03	1.71
C.V.	0.41	0.53	0.39	0.56	1.33	0.46	0.49
Fine tailings (*n* = 30)							
Min.	22.67	3.07	12.55	0.02	0.02	0.51	0.36
Max.	53.33	17.34	23.75	3.45	0.42	1.37	2.77
Mean	41.89	7.99	17.29	1.41	0.11	1.12	1.59
C.V.	0.31	0.51	0.19	0.63	1.50	0.35	0.62

Table 5. Potentially toxic elements (mg/kg), pH and soluble fraction (SF) (wt%) in the waste, depending on the grain size

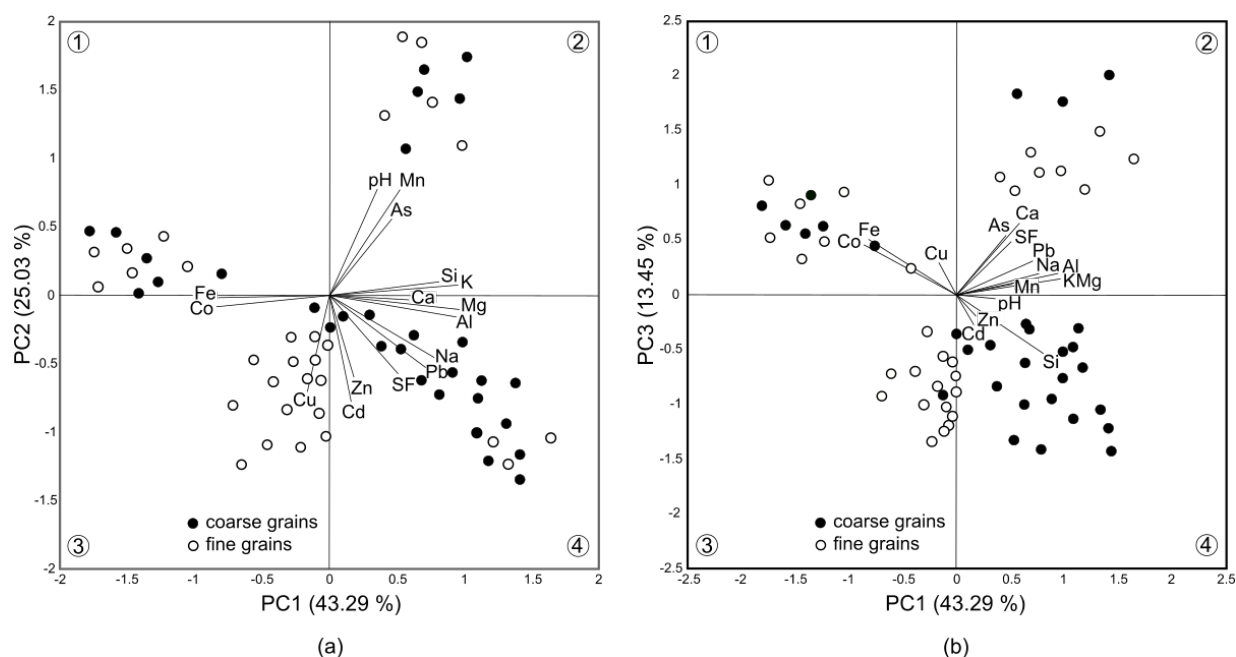|	Mn	Co	Cu	Zn	Cd	Pb	As	pH	SF
Coarse tailings (*n* = 30)									
Min.	76	16	99	91	0.09	289	97	2.33	3.22
Max.	301	59	1204	933	1.95	3036	379	3.89	29.38
Mean	160	37	511	402	1.03	1397	201	2.86	11.22
C.V.	0.36	0.52	0.64	0.72	0.74	0.94	0.46	0.33	0.66
Fine tailings (*n* = 30)									
Min.	109	25	177	122	0.35	295	145	2.21	6.66
Max.	277	70	1676	2099	3.76	3117	584	4.01	40.00
Mean	148	51	786	901	2.02	1276	209	2.93	10.80
C.V.	0.40	0.15	0.67	0.70	0.65	0.71	0.86	0.12	0.65

Figure 2. The combined plot of scores and loadings on principal components PC1, PC2, and PC3.

The waste in an abandoned tailings pond may be considered as a sum of solid-liquid systems. Their characteristics vary depending on several parameters such as the grain size and mineral phases of the detritus, water abundance and its pH, intensities of oxidation and liquid evaporation, precipitation of secondary minerals, and the acid mine drainage (AMD) productivity. The change of these parameters produces various types of local environments within the tailings pond. PCA results suggest that, in the specific case of the Straja Valley waste deposit, the different local environments may be assigned to two main types: (i) environments poor in water (mainly pore water) defined by low evaporation and limited precipitation of secondary minerals (negative PC3); (ii) water-rich environments characterized by intense evaporation and precipitation of secondary minerals (positive PC3) (Fig. 2b).

In figure 2a, the negative correlations between Fe and Co on one hand and Si, K (but also Mg and Al), on the other hand, suggest two categories of detritus, as follows: (i) pyrite-rich detritus (negative PC1); (ii) detritus showing a high abundance of silicates (quartz, sericite/muscovite, chlorite) and sphalerite ± galena (positive PC1). Nonetheless, when collected from the dam of the waste deposit (positive PC2), it seems like the two detritus types are not different in terms of the grain size. On the contrary, the samples collected from the beach (negative PC2) show distinct mineralogical and granulometric properties. Hence, the pyrite-rich waste appears especially as fine grains on the beach (sector 3 in figure 2a), probably because of a late settlement. On the other side, when the waste of the beach initially consists mainly of silicates + sphalerite ± galena as coarse grains, secondary, soluble minerals trapping Pb (also, partially Zn and Cd) in their structure may appear (sector 4 in figure 2a). According to data in table 1, these minerals may be natrojarosite, plumbojarosite, and gypsum (Smuda et al., 2014; Drahota et al., 2016). Despite a similar variant granulometry with the waste in the sector 1 of the figure 2a, the samples in sector 2 show specific properties. The geochemical properties of the secondary minerals seem to be controlled by pH, whose variation may favor the trap of Mn in gypsum and goethite coatings formed onto the primary minerals (Hammarstrom et al., 2005; Smuda et al., 2014). Also depending on pH, As may enter the mineral structure of copiapite, jarosite, and goethite (Hiller et al., 2012; Parviainen et al., 2012; Jamieson et al., 2015; Root et al., 2015; Courtin-Nomade et al., 2016).

Figure 2b shows the role of water and associated processes (evaporation, secondary mineral precipitation) in the evolution of both pyrite-rich and silicate-rich + sphalerite ± galena types of waste. The negative PC3 explains the water-poor environments, set up during dry periods. In this case, the pyrite-rich tailings consist mainly of fine grains of pyrite (sector 3 in figure 2b), while the silicate-rich waste comprises coarse grains of quartz (sector 4 in figure 2b).

The environments involving relative abundant water seems to control positive PC3. The aqueous environments appear as a result of the rainy periods when water accumulates either as puddles over the waste beach or as pore-water within the tailings. As expected, the scores of samples rich in pyrite (sector 1

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in figure 2b) show their strong relation with Fe and Co. Nonetheless, the aqueous environment and the presence of goethite in the waste (Table 1) suggest that this mineral may be partially responsible for the Fe distribution. The assumption appears to be supported by the weak correlation between Fe and Cu, despite the presence of the latter within the pyrite structure. Sector 1 in figure 2b groups mainly the samples collected from the dam of the tailings pond, indicating that the aqueous environment consists of pore-water trapped within the detritus.

The geochemical properties of the samples in sector 2 of figure 2b are in close relation with the soluble fraction loading. This indicates a water-rich environment that undergoes intense evaporation, leading to the precipitation of secondary minerals, i.e., especially highly soluble hydrated sulfates. When accumulating as puddles, the aqueous solutions also favor the settlement of the very fine fraction, which consists mainly of clay minerals. In connection with the minerals identified through XRD, the strong positive correlations between the soluble fraction and Pb, Al, Mg, Ca, Na may be intimately tied up to the secondary minerals. The latter have appeared at the expense of waste rich in silicates + sphalerite (±galena) and account partially for Pb, Ca, Mg, and Na distribution within the waste, as follows: (i) Pb may be related to jarosite, goethite, gypsum and clay minerals that can trap it within their structures (Graupner et al., 2007; Hayes et al., 2012; Smuda et al., 2014; Courtin-Nomade et al., 2016; Drahota et al., 2016); (ii) the Al loading is explained by the presence of alunite and clay minerals (iii) part of the Mg amount seems to be in relation with magnesiocopiapite and illite-montmorillonite; (iv) gypsum and clay minerals are responsible for Ca distribution; (v) the precipitation of natrojarosite and settlement of illite-montmorillonite explain the Na scores. As concerns arsenic, it shows no correlation with the soluble fraction (Pearson correlation coefficient of less than 0.1). However, the PCA biplot in figure 2b suggests the control of fine grains over arsenic; the fine mineral grains that may trap As within the structure are galena (Root et al., 2015) and, when present, pyrite (Moncur et al., 2005; Romero et al., 2007; Savage et al., 2008).

5. ENVIRONMENTAL RISKS RELATED TO AIRBORN TRANSPORT

The procedures for calculating the wind-blown sand transport (US Army Corps of Engineers, 2012) were adapted to determine the threshold wind speed that may initiate waste transport toward the surrounding areas. Therefore, the threshold wind speed was determined based on its mathematical relationship with the gravitational acceleration, density of air, grain size, and the density of waste. The calculations were performed for the grain classes described in the present study, namely coarse- (> 0.25 mm) and fine-grained waste (< 0.25 mm). The densities were determined using the method described in the section Materials and methods, for the types of waste identified through the multivariate statistic approach. Data in table 6 show the shear wind velocities assumed to trigger the waste removal from the surface of the tailings pond when long drought periods occur.

Table 6. Threshold wind speeds (m/s) resulting in the waste transport

	Ground	10 m height
CG (Q)	> 0.27	> 7.10
CG (Sil.+Sp±Gn)	> 0.28	> 7.30
FG (Py)	< 0.29	< 7.60
FG (Sil.+Sp±Gn)	< 0.30	< 7.90

CG (Q) – coarse-grained waste rich in quartz ($\rho = 2.63$ g/cm^3); CG/FG (Sil.+Sp±Gn) – coarse-/fine-grained waste rich in silicates (including quartz), sphalerite (± galena) ($\rho = 2.79/3.25$ g/cm^3); FG (Py) – fine-grained waste rich in pyrite ($\rho = 3.01$ g/cm^3).

The threshold wind speeds were also calculated for 10 m above ground, i.e., the height at which the meteorological observations are usually carried out. These data suit the moderate breeze of the Beaufort wind scale for land areas (in between 5.8 and 8.3 m/s) (RMetS, 2015). This fact, correlated with the results of multivariate statistics (Fig. 2), leads to the following assumptions concerning the wind-driven pollution of the surrounding areas by the waste of the tailings pond, during long periods of drought:

(i) At wind speeds that exceed 7.1-7.3 m/s (moderate breeze), the coarse fraction rich in quartz or silicates (including quartz) + sphalerite ± galena is removed from the surface of the waste deposit. Quartz-rich waste (Fig. 2b, sector 4) only produces mechanical pollution. Though, the second type of detritus may also cause pollution with toxic elements (Pb and partially Zn, Cd), because of sphalerite (± galena) and associated secondary minerals (Pb-jarosite, Mg-copiapite, goethite, apjohnite, clay minerals) (Fig. 2a, sector 4).

(ii) The pyrite-rich fine fraction is driven away from the waste deposit during moderate breeze or lower wind speeds (less than 7.6 m/s). It can be presumed that the spread and settlement of fine-grained pyrite in the surrounding areas represent an environmental risk because of its large specific

surface area, which increases the susceptibility of reacting at weathering factors. The latter may trigger the pyrite oxidation, followed by an increase of the environment acidity and release of Cu, Zn, and Cd, as suggested by figure 2a (sector 3).

(iii) The removal of the waste consisting of fine-sized grains of silicates in general (including quartz) + sphalerite ± galena occurs at quite similar wind speed as for pyrite-rich fine tailings, i.e., a wind velocity less than 7.9 m/s. Data in figure 2b (sector 2) indicate a risk of environmental pollution with Pb and As accumulated in galena, but also by secondary soluble minerals such as Pb-jarosite, Mg-copiapite, apjohnite, and goethite.

6. CONCLUSIONS

In the present study, the mineralogical and geochemical properties of two grain-size classes of waste were considered namely waste tailings larger than 0.25 mm (named coarse grains) and smaller than 0.25 mm (named fine grains).

Among the general features of the waste is the presence of several secondary minerals (Na- and Pb-jarosite, Mg-copiapite, gypsum, alunite, apjohnite, and goethite), which are more abundant in the tailings of the waste deposit beach. They were generated by the weathering of the primary minerals, resulted from the metallic ores (especially pyrite) and host rocks (micas, chlorite). The geochemical patterns of the tailings samples depend on their location on the waste deposit surface and the abundance of soluble fraction, which consist mostly of hydrated sulfates. The Si content in the beach waste samples is higher than in the dam slope, because of the wind-driven quartz accumulated as thin layers onto the tailings pond surface. The samples collected from the dam show lower contents of Al and Mg (also Na and K, to some extent). This is due to phyllosilicates susceptibility to removal by runoff and the depletion of secondary minerals. Higher Fe content on the dam slope results from the pyrite lower mobility, during runoff. The Cu, Zn, Cd, and Pb contents are higher in the beach waste. This may be related to the capacity of some secondary minerals (jarosite, Mg-copiapite, apjohnite, goethite, gypsum, illite-montmorillonite, and kaolinite) to trap these elements in their structure.

Broadly, the fine- and coarse-grained waste show similar geochemical properties. Nevertheless, the coarse-grained tailings are more abundant in silica (due to quartz), while the fine-grained waste has higher amounts of Fe, Cu, and Zn. This is because of the higher abundance of fine-grained pyrite (+sphalerite), as a result of mass loss during metal extraction, in the processing plant.

The Principal Component Analysis (PCA) indicated the factors that control the textural, mineralogical, and geochemical patterns of the waste; these factors are: (i) the tailings location in the waste deposit (either on the beach or dam slopes); (ii) the amount of pyrite within the waste (either pyrite-rich tailings or waste rich in silicates + sphalerite ± galena); (iii) the water abundance, which generates poor-water environments (pore water) or rich-water environments (water in the puddles accumulated on the beach).

PCA also suggested some patterns related to the texture and type of the waste, as follows: (i) samples collected from the dam present variable grain-size; (ii) pyrite-rich tailings (with higher contents of Cu, and partially Co, Zn, Cd) from the beach appears as fine grains; (iii) if the coarse-grained waste of the beach is rich in silicates (+ sphalerite ± galena), it is associated with secondary minerals (Na-jarosite, Pb-jarosite, and gypsum) that may trap Pb, Zn, and Cd in their structure; (iii) when the latter type of waste is dominated by quartz, it appears as a coarse-grained detritus, which is not associated with secondary minerals; (iv) whether the waste from the beach is rich in silicates but is fine-grained, it is associated with soluble secondary minerals (Na-jarosite, Mg-copiapite, gypsum, alunite) and clay minerals that may trap Pb and As in their structure.

The estimation of the threshold wind speed that may initiate the waste transport toward the surrounding areas indicated some potential environmental risks namely: (i) the winds that exceed the moderate breeze may produce a mechanical pollution with quartz and chemical pollution with Pb, Zn, Cd, trapped in the structure of primary minerals (sphalerite ± galena) and secondary minerals (Pb-jarosite, Mg-copiapite, goethite, apjohnite, clay minerals); (ii) the winds less intense than a moderate breeze may transport into the surrounding areas fine-grained pyrite (and Cu, Zn, Cd within) or secondary minerals that accumulate Pb and As in their structure (Pb-jarosite, Mg-copiapite, apjohnite, and goethite).

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