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Metal extractability in acidic and neutral mine tailings from the Cartagena-La Unión Mining District (SE Spain)

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Abstract

Mine tailings are ubiquitous in the landscapes of mined areas. Metal solubilities were compared in two chemically distinct mine tailings from the old Mining District of Cartagena-La Unión (SE Spain). One of the tailings was acidic (pH 3.0) with 5400 mg/kg Zn, 1900 mg/kg As and 7000 mg/kg Pb. The other was neutral (pH 7.4) with 9100 mg/kg Zn, 5200 mg/kg Pb and 350 mg/kg As. In samples from the acidic tailings, more than 15% of the Zn and 55% of the Cd were extractable with 0.1 M $NaNO_3$, and distilled water. In the neutral tailings, using the same reagents, less than 1% of the metals were extractable. A sequential extraction procedure revealed that the sum of the residual and the Fe oxide fractions of Cu, Zn and Pb comprised 80–95% in the acidic tailings and 70–90% in the neutral tailings. The acidic mine tailings had a higher metal solubility, resulting in more metal leaching in the short-term, but also a higher fraction of inert metal. In contrast, in the neutral tailings, the metals were evenly distributed between, oxides and the residual fraction. This implies lower metal mobility in the short-term, but that metal mobility may increase in the long-term. When applied to mine tailings, sequential extractions may provide misleading results because the strong cation exchange capacity of some extractants may induce pH changes and thereby significantly change metal solubility.

1. Introduction

The Cartagena-La Union Mining District was an important mining area for more than 2500 a until mining activity ceased in 1991. Base metals were smelted from sulfide minerals that included galena and sphalerite. At present, more than 40 mine tailings piles cover approximately 160 ha in this area (Martínez-Orozco et al., 1993). These contain high concentrations of toxic metals and present a human and environmental health risk due to exposure of wind-borne dust.

The toxicity and plant uptake of metals depend on their speciation in soil (Zhang et al., 2001). Soil extractions with water, dilute salt solutions or chelating agents may approximate the fractions of soil metals that are available for uptake by plants (Ernst, 1996). Soil extraction schemes can be classified as

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single or sequential. Traditionally, single extractions have been used to assess the fertility of croplands (Rauret, 1998).

Sequential extractions consist of a series of steps in which extractants with increasing solubilisation potential are applied successively to assess the proportions of metals that are associated with various soil components (Tessier et al., 1979; Zeien and Brümmer, 1989). However, many studies have highlighted problems with extracting reagents, such as insufficient selectivity (La Force and Fendorf, 2000), or the redistribution of analytes during the procedure (Gómez-Ariza et al., 1999; Calmano et al., 2001). Most sequential extraction procedures were developed for agricultural soils, usually with low to moderate metal concentrations (Calmano et al., 2001). Compounds that are highly soluble in a given extractant, but are not common in the soils for which the procedure was developed, may interfere with the extraction of metals from other soil types or highly polluted soils (Gleyzes et al., 2001). Sequential extraction procedures have also been applied to As (Méndez and Armienta, 2003; Ko et al., 2003; Wenzel et al., 2001). Unlike most metals, As in the environment occurs predominantly as an anion, rather than a cation, for which the sequential extractions were developed.

Numerous authors have applied sequential extractions to highly metal polluted soils. Some authors have modified the sequential extraction proposed by Tessier et al. (1979) to study metal partitioning in industrial sites (Li and Thornton, 2001), heavy metal polluted sediments (Gómez-Ariza et al., 1999) or mine tailings (Fanfani et al., 1997). The sequential extraction scheme proposed by Zeien and Brümmer (1989) has been applied to metal polluted agricultural soils (Fischer et al., 1998), soils affected by smelter dust deposition (Tandy et al., 2004), urban soils (Thuy et al., 2000) and mine tailings (Kim et al., 2002). Several authors have used conventional or slightly modified extraction schemes to investigate As speciation in highly polluted soils (Méndez and Armienta, 2003; Ko et al., 2003; Wenzel et al., 2001).

The aim of this work was to study the solubility and solid phase fractionation of metal(loid)s in two mine tailings with contrasting pH values from the Cartagena-La Union Mining District in southern Spain. Several single extractions were compared to the sequential extraction scheme of Zeien and Brümmer (1989). The results of the extractions were examined with a view to determining the advantages and limitations of applying such extractions to mine tailing materials.

2. Materials and methods

2.1. Sampling site

The Cartagena-La Union Mining District is located in the Murcia Region (SE Spain). The area of the Mining District is approximately 50 km^2 and includes five cities with a total population of 20,000. The climate is typically Mediterranean with an average rainfall of 250–300 mm/year, concentrated in spring and autumn. The annual mean temperature is 18 °C. The topography and semi-arid climate result in a hydrology characterised by short streams (<20 km length) with intermittent flow and fast drainage that promotes erosion. The natural vegetation consists of thickets containing xerophitic species.

2.2. Soil sampling

Two mine tailings were studied. The “Belleza” mine tailings, are near the town La Unión. Erosion has already carried part of the tailings into two nearby creeks. Two schools are within 500 m of the base of the tailings. The surface of the tailings is covered with a hardpan, which contains visible salt crystals. The “El Gorguel” mine tailings are located along the dry “Gorguel” river. The surface horizons of the tailings consist of sandy sediments without structural aggregates. Conesa et al. (2006) gives more details of the sampling locations. Henceforth, the Belleza and El Gorguel tailings are referred to as the “acidic tailings” and “neutral tailings”, respectively.

Samples were taken from the upper 40 cm at 15 separate pits that were dug at regular intervals, at least 8 m apart, over each tailings pile. All samples were mixed to give one homogenised sample per zone. The samples were air dried, sieved to less than 2 mm and stored in plastic bags prior to laboratory analysis.

2.3. Analytical methods

The pH of a suspension in H_2O with a tailings: water ratio of 1:2.5 (g:mL) was measured using a pH Meter (Omega) Metrohm. Total element concentrations were determined using X-ray fluorescence (Spectro X-Lab 2000). Soluble metal(loid)s were extracted with 0.1 M $NaNO_3$ at a 1:2.5 tailings: solution ratio (g:mL) (FAL, RAC, FAW, 1996) and with H_2O at a 1:5 tailings: water ratio (g:mL) (Ernst, 1996). There were three replicates per sample. For both extractions, the samples were shaken for 2 h, centrifuged for 10 min at 4000 rpm, and filtered through 0.45 μm cellulose acetate filters (Sartorius). The filtered extracts were analysed for Cu, Zn, Cd, Pb and As by flame atomic absorption spectrometry (SpectraAA 220/FS, Varian). The detection limits in these extracts were 0.1 mg/L for all the elements except As, where the detection limit was 0.5 mg/L. The high salt content of the extracts limited the sensitivity. To determine the mineral composition of the two tailings, sub-samples were ground and analysed by X-ray diffraction, using a D4 Endeavor spectrometer using the software DIFFRAC plus EVA V8.0 (Broker AXS. INC. United States).

For the sequential extraction, the procedure of Zeien and Brümmer (1989) was followed. Table 1 gives the definition of the fractions in this scheme as well as the components of the extracting solutions. All suspensions were centrifuged at 2500 rpm for 10 min and passed through Schleicher & Schüll 790 1/2 filter paper. The elements (Cu, Zn, Cd, Pb and As) extracted in steps 1–6 were measured by flame atomic absorption spectrometry (SpectraAA 220/FS, Varian). The detection limits in these extracts were 0.01 mg/L for Cu, Pb, Zn and Cu, and 0.5 mg/L for As. The residual fraction (step 7) was analysed by X-ray fluorescence (Spectro X-Lab 2000). Six sub-samples of 2 g from each tailing sample were analysed.

Table 1
Chemical interpretation and operational definition of the fractions within the sequential extraction scheme (following Zeien and Brümmer, 1989)

Fraction	Chemical interpretation	Extractant	Duration
F1	Mobile (water soluble and easily exchangeable metals)	1 M NH_4NO_3	24 h, 20 °C
F2	Easily mobilizable (specifically adsorbed, bound to $CaCO_3$)	1 M NH_4–acetate (pH 6)	24 h, 20 °C
F3	Bound to Mn oxides	0.1 M NH_2OH–HCl + 1 M NH_4–acetate (pH 6)	30 min, 20 °C
F4	Bound to organic matter	0.025 M NH_4EDTA (pH 4.6)	90 min, 20 °C
F5	Bound to amorphous Fe oxides	0.2 M NH_4–oxalate (pH 3.25)	4 h in the dark, 20 °C
F6	Bound to crystalline Fe oxides	0.1 M ascorbic acidic + 0.2 M NH_4–oxalate (pH 3.25)	30 min at 96 °C
F7	Residual fraction	X-ray fluorescence	

3. Results and discussion

3.1. Characterisation of the tailings

Table 2 shows the pH of the saturated extract and total elemental concentrations in the two mine tailings. The pH was 3.0 in the acidic tailings and 7.4 in the neutral tailings. Both tailings had high Fe concentrations, especially the acidic tailings (26%). Silicon occurred at concentrations around 10%. Aluminium and S exceeded 1% in both tailings, as did Ca in the neutral tailings. The Cu, Zn, Cd and Pb contents were high in both tailings. The highest values for Pb and As occurred the acidic tailings while the neutral tailings had the highest Zn and Cd concentrations.

3.2. Mineralogy

The acidic mine tailings was composed of quartz (SiO_2), magnetite (Fe_3O_4), goethite (α-FeOOH), beudantite ($(Pb(Fe_{2.54}Al_{0.46})(As_{1.07}O_4)(S_{0.93}O_4)(OH)_6)$), vermiculite 2 ITM RG ($Mg_3Si_4O_{10}(OH)_2$), sphalerite (ZnS), faujasite ($H_{7.7}Al_{42.56}Si_{139}O_{345.6}$) and gypsum

Table 2
Concentration of major elements and metal(loid)s in the two mine tailings

Element	Unit	Acidic tailings	Neutral tailings
pH[a]	–	3.0	7.4
Al	%	2.0(0.1)	4.2(<0.1)
Si	%	8.3(0.3)	13(0.3)
S	%	2.7(<0.1)	3.0(<0.1)
Ca	%	0.8(<0.1)	3.0(0.1)
Fe	%	26(0.8)	11(<0.1)
As	mg/kg	1900(33)	350(7.2)
Cd	mg/kg	8.8(0.4)	34(0.7)
Cu	mg/kg	380(14)	84(4.5)
Pb	mg/kg	7000(130)	5200(50)
Zn	mg/kg	5400(100)	9100(34)

Values in brackets are standard deviations ($n = 3$).

[a] Geometric mean. The differences between the samples were <0.1, the detection limit of the apparatus.

Table 3
Metals extracted by 0.1 M $NaNO_3$ and H_2O

Reagent	Tailing	Cu	Zn	Cd	Pb
0.1 M $NaNO_3$	Acidic	6.7(0.2)	1000(72)	5.3(0.1)	9.4(0.2)
	Neutral	<0.3	1.9(0.1)	<0.3	<0.3
H_2O	Acidic	7.3(0.1)	990(11)	5.0(0.1)	12(0.1)
	Neutral	<0.5	2.3(0.2)	<0.5	<0.5

Values in brackets are standard deviations ($n = 3$). All data are mg/kg. Arsenic was below the detection limit.

($CaSO_4 \cdot 2H_2O$). Beudantite is a typical mineral in gossans, which results from the intensive oxidation of surface sulfide deposits. It acts as a natural sink for Pb and As (Nieto et al., 2003).

In the neutral tailings, only three minerals were identified: quartz, gypsum ($CaSO_4 \cdot 2H_2O$) and chlorite ($(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$). Despite a Fe concentration of 10%, no Fe mineral was detected. This indicates that the Fe was probably present as a finely dispersed amorphous oxide.

3.3. Single extractions with 0.1 M $NaNO_3$ and H_2O

Table 3 summarises the results of the two single extractions using 0.1 M $NaNO_3$ and H_2O. In 0.1 M $NaNO_3$ extracts of the acidic tailings, the highest concentrations were obtained for Zn (1000 mg/kg). However, Cu, Cd and Pb also had substantial soluble fractions. As expected, the $NaNO_3$ and H_2O extracts of the neutral tailing contained much lower metal concentrations, due to the higher pH of the material. Copper, Cd and Pb were below detection limits (<0.50 mg/kg).

The water-extractable Cu, Zn, Cd and Pb concentrations were close to the respective $NaNO_3$ extractable metal concentrations. This indicates that results from these extractants can be compared directly for these types of materials. Arsenic was below the detection limit in all the cases, with acidic and neutral tailings.

3.4. Sequential extractions

In the acidic tailings, the average recovery for the sum of the seven fractions (Table 4) compared to the total analysis (Table 2) was 89.1% for Cu, 95.6% for Zn, 96.9% for Cd, 74.3% for Pb and 78.7% for As. In the neutral tailings, the recoveries were 101.3% for Cu, 111.4% for Zn, 92.8% for Cd, 87.0% for Pb and 128.1% for As. These values were similar to those reported by other authors (Widerlund et al., 2005). The high number of replicates ($n = 6$) resulted in a high reproducibility of the results. The highest relative standard deviations (calculated from Table 4) occurred in the 6th step, except for Zn (3rd and 4th steps) and Pb (1st and 2nd steps). These steps were coincidental with low concentrations and thus the high variability did not significantly affect the final results.

Most of the discussion is based on percentages because it is necessary to compare two materials with different total concentrations and investigate the mechanisms of solubilization, rather than individually evaluate the possible toxicity of each tailings. Except for As, the most soluble element fraction (F1) was higher in the acidic tailings (Fig. 1 and Table 5). The percentages of Cu and Cd extracted

Table 4
Concentration of metals extracted in each step of the sequential extraction and its total sum

Tailings	Element	Step							Sum of all the steps
		Mobile (F1)	Easily exchangeable (F2)	Mn oxides (F3)	Org. matter (F4)	Amorphous Fe oxides (F5)	Crystalline Fe oxides (F6)	Residual (F7)	
Acidic	Cu	16.9(0.62)	0.53(0.06)	<0.01	3.62(0.13)	26.9(0.66)	12.4(0.98)	278(27.0)	339(27.2)
	Zn	1110(25.6)	10.3(1.56)	27.9(8.58)	30.4(12.0)	264(24.8)	986(65.6)	2740(205)	5170(237)
	Cd	6.14(0.25)	0.21(0.04)	<0.01	<0.01	0.65(0.07)	0.54(0.11)	0.99(0.32)	8.53(0.33)
	Pb	436(58.8)	24.9(5.33)	141(16.6)	332(24.7)	772(66.2)	399(44.3)	3090(314)	5200(378)
	As	25.8(2.15)	37.4(1.02)	34.6(1.47)	27.2(2.69)	124(7.30)	620(55.9)	627(50.4)	1500(83.8)
Neutral	Cu	1.13(0.09)	3.25(0.39)	<0.01	5.14(0.19)	36.5(0.60)	3.05(0.88)	36.1(2.14)	85.1(2.36)
	Zn	173(9.69)	1300(28.5)	355(5.71)	1020(23.8)	4290(133)	970(216)	2030(108)	10100(141)
	Cd	4.81(0.12)	9.66(0.07)	1.60(0.04)	1.96(0.06)	4.40(0.14)	1.09(0.39)	8.03(0.48)	31.6(0.38)
	Pb	3.23(0.39)	302(16.3)	351(16.3)	315(16.2)	572(56.2)	350(19.5)	2630(182)	4520(215)
	As	21.2(1.44)	35.3(1.40)	32.1(1.47)	23.0(2.36)	137(6.89)	105(15.7)	95.3(18.5)	448(29.2)

Values in brackets are standard deviations ($n = 6$). All data are mg/kg and have been rounded to three significant digits.

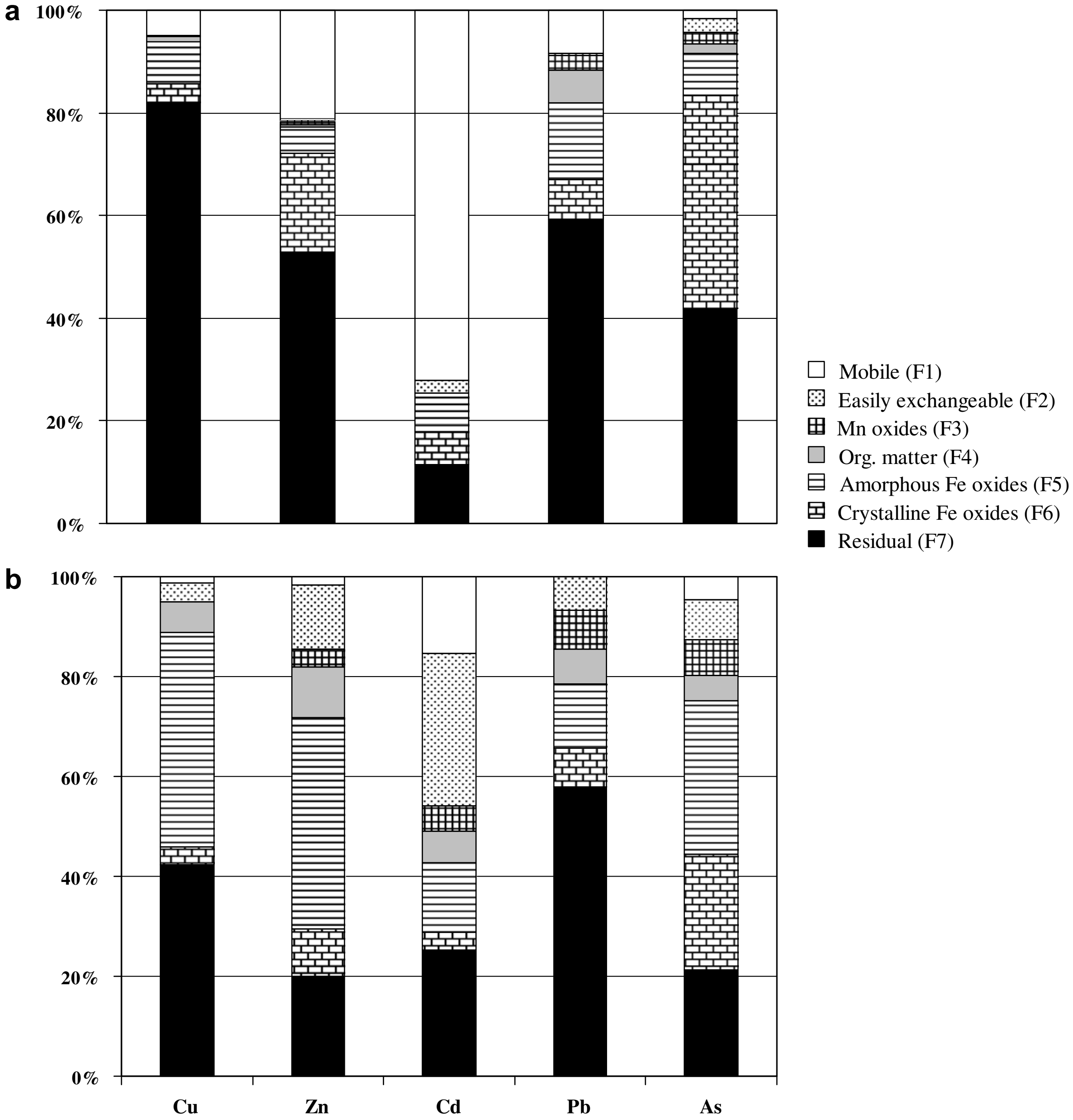

Fig. 1. The distribution of Cu, Zn, Cd, Pb and As (average of six replicates) in the sequentially extracted acidic (a) and neutral (b) mine tailings.

in step F1 (5% and 72%, respectively) were around 4 times higher in the acidic tailings than in the neutral tailings. These differences were even larger for Zn and Pb. However, in the following F2, F3 and F4 steps, the percentages of elements extracted were higher in the neutral tailings than in the acidic tailings.

Around 80% Cu occurred in the residual fraction of the acidic tailings. In the neutral tailings this fraction was only 42%, but an additional 46% occurred in the two Fe oxide fractions (F5 + F6). A similar pattern was found for Zn with a high percentage (53%) in the residual fraction in the acidic tailings compared to the neutral one (20%) and a similar amount (52%) to Cu in the two Fe oxide phases (F5 + F6).

Most of the As was in the three most inert fractions (F5 + F6 + F7), around 90% in the acidic

Table 5
Percentages of metal extracted in each step of the sequential extraction

Tailings	Element	Step						
		Mobile (F1)	Easily exchangeable (F2)	Mn oxides (F3)	Org. matter (F4)	Amorphous Fe oxides (F5)	Crystalline Fe oxides (F6)	Residual (F7)
Acidic	Cu	4.98	0.16	<0.01	1.07	7.93	3.65	82.2
	Zn	21.4	0.20	0.54	0.59	5.10	19.1	53.1
	Cd	72.0	2.48	<0.01	<0.01	7.59	6.35	11.6
	Pb	8.39	0.48	2.71	6.40	14.9	7.67	59.5
	As	1.73	2.50	2.31	1.82	8.26	41.5	41.9
Neutral	Cu	1.33	3.81	<0.01	6.04	42.9	3.59	42.4
	Zn	1.71	12.8	3.51	10.1	42.3	9.57	20.1
	Cd	15.3	30.6	5.07	6.22	14.0	3.45	25.4
	Pb	0.07	6.68	7.77	6.96	12.7	7.73	58.1
	As	4.73	7.88	7.16	5.13	30.5	23.3	21.3

The numbers have been rounded to three significant digits.

tailing and 70% in the neutral one. Arsenic was the only element with a higher percentage of the most soluble fraction (F1) in the neutral tailings (4.73%) than in the acidic tailings (1.73%). The prevalent forms of As in the environment are the inorganic oxyanions of As(III) and As(V) (Mahimairaja et al., 2005). The pH dependence of the solubility was therefore consistent with the expectation that the solubility of anions generally increases with increasing pH, whereas that of cations decreases.

Results from sequential extractions should be evaluated with care. For example, the fraction extracted with EDTA in the 4th step of the Zeien and Brümmer (1989) procedure is normally attributed to elements bound by organic matter. This interpretation is questionable in the case of mine tailings, because the organic matter content (<0.5%) is very low (Conesa et al., 2006). For Pb this fraction (F4) was 6–7%. This fraction probably corresponds to Pb adsorbed onto mineral surfaces because EDTA is an efficient extractant for Pb from polluted soils. Nowack et al. (2006) reported that EDTA extracts 40–100% of total Pb from soils, even at high Pb concentrations.

The sum of the percentages of the first two fractions (F1 + F2) was similar for Cu (5–6%) and Pb (7–9%) in both tailings, although the F1 was always much higher in the acidic tailings. This did not occur for Cd and Zn, although there was a higher fraction of the metals in the F2 step in the neutral tailings compared to the acidic tailing. This may have occurred because the first step was not pH buffered and therefore the extraction occurred at acidic pH for the acidic tailings and neutral pH for the neutral tailings. The second step was buffered at pH 6, resulting in a pH increase in the acidic tailings and a pH decrease in the neutral tailings. García et al. (2005) also reported this effect using a different sequential extraction procedure on similar tailings from the Cartagena-La Union Mining District. They found that higher metal percentages occurred in the most soluble fraction of the neutral tailings compared to the acidic tailings. These authors hypothesised that in the acid tailings most of the soluble metal had already leached out. In the present study, the mobility was higher at pH 3 for all elements except As. These conflicting results may be due to the use of different reagents in the first step of the sequential extraction procedure. The NH_4OAc (pH 5) used by García et al. (2005) in this first step, would have acted as a buffer and the extraction took place at this pH. For the acidic tailings, this would have resulted in a pH increase and therefore reduced solubility of metals while for the neutral tailing this resulted in a decrease in pH of 2 units and therefore increased solubility. This demonstrates the need for caution when interpreting results from sequential extractions where the pH at which the extraction occurs is different from that of the native soil.

In the acidic tailings, both the most soluble (F1) and the residual fractions (F7) were higher for Cu and Zn compared to the neutral tailings. Lead was similarly distributed in both tailings. The sum of the three most environmental inert fractions (F5 + F6 + F7) was 70–95% for Cu, Zn, Pb and As in both mine tailings, indicating that large fractions of the metal(loid)s are strongly bound to the matrix. The acidic mine tailings are therefore characterised, paradoxically, by a high solubility and long-term persistence of Cu, Zn and Pb. Cadmium is soluble (more than 50% in F1 + F2 + F3) and present at low percentages in the F7 residual fraction (11% in the acidic and 25% in the neutral).

For most metal(loid)s and most soluble fractions, using concentrations (Table 4) instead of percentages gives the same result, however, some differences are observed especially for As and Cu. For these two elements, the largest difference in total concentrations is observed (the acidic tailings had 5 times more As and 4.5 times more Cu, but 4 times less Cd). For As, the concentration in F1 was higher in the acidic tailings although the percentage was lower. This shows that for an actual risk assessment of a specific site the concentrations should also be considered while for an understanding of the processes the percentages may be more meaningful.

3.5. Comparison between metals extracted with H_2O, 0.1 M $NaNO_3$, and 1 M NH_4NO_3

Table 6 gives a comparison of the metal extractability in the two tailings by the three extractants H_2O, 0.1 M $NaNO_3$, and 1 M NH_4NO_3. The latter is the extractant used in the first step of the sequential extraction. The three extractants solubilised approximately equal amounts of Zn from the acidic tailings. More Cu and Cd were extracted by 1 M NH_4NO_3 than by water and 0.1 M $NaNO_3$. Only 1 M NH_4NO_3 extracted significant amounts of Pb. In the neutral tailing, 1 M NH_4NO_3 extracted 15% of the total Cd and 1.7% of the total Zn. The extractability of these metals in 0.1 M $NaNO_3$ and H_2O was below detection limits.

For recalcitrant metals (e.g. Pb) and other elements in pH-conditions that favour strong binding (high pH), only the strongest extractant for “mobile” elements, 1 M NH_4NO_3, yielded significant concentrations. This was the only extractant that solubilised Pb from the acidic tailings. The higher concentration in the extract with NH_4 may indicate that the solubility was not limited by a mineral phase but by adsorptive processes. Ammonium is not able to complex metals. Its solubilising capacity is due to cation exchange with metals adsorbed on mineral surfaces or clays. Water and 0.1 M $NaNO_3$ yielded similar amounts of extracted elements, indicative of the weak extraction power of 0.1 M $NaNO_3$.

Table 6
Comparison between the percentage of mobile metals extracted with the two single extractions applied (0.1 M $NaNO_3$ and H_2O) and the most mobile fraction from the sequential extraction (1 M NH_4NO_3)

Metal	Acidic tailings			Neutral tailings		
	0.1 M $NaNO_3$	H_2O	1 M NH_4NO_3	0.1 M $NaNO_3$	H_2O	1 M NH_4NO_3
Cu	1.8	1.9	5.0	<1	<1	1.3
Zn	19	18	21	<1	<1	1.7
Cd	61	56	72	<1	<1	15
Pb	<1	<1	8.4	<1	<1	<1

Values are % of total metals.

The risk assessment of mining areas requires an accurate characterisation of the wastes. This characterisation reveals situations where high concentrations of elements may leach or be taken up by the biota. In the present study, the acidic tailings pose a higher risk than the neutral tailings for ground and surface waters due to the higher metal solubility at low pH. This high solubility also implies high bioavailability. Nevertheless, the low pH of the tailings, or toxicity due to high metal(loid) concentrations, prevents the establishment of vegetation thereby reducing ingestion into the food chain via plant uptake. The neutral tailings provide a more favourable environment for plant colonisation. Therefore, despite having a lower metal(loid) leaching risk, vegetation may facilitate the entry of elements into the food chain. However, vegetation may prevent erosion and dust, and thus reduce the direct consumption of the tailings through air born particles. Conesa et al. (2007) studied the dynamics of plant communities in the same tailings and observed more stable plant populations in the neutral tailings compared to the acidic tailings. Previous studies of these plant communities have found low metal concentrations in plant tissues: $<1000\ \mathrm{mg\,kg^{-1}}$ for Zn and $<500\ \mathrm{mg\,kg^{-1}}$ for Pb, and $<16\ \mathrm{mg\,kg^{-1}}$ for Cu (Conesa et al., 2006).

A short-term remediation program (e.g. lime amendments) would be suitable for the acidic materials to reduce the solubility of the metal(loid)s contained therein. The neutral tailings, in spite of the lower metal(loid) solubility, may pose a long-term risk of leaching if conditions change and through plant growth and uptake, which is more favourable on neutral tailings..

4. Conclusions

The analyses revealed high concentrations of Cu, Zn, Cd and As in the two investigated types of mine tailings from the Cartagena-La Union Mining District. The extraction analyses showed that Cd and Zn were easily mobilized by the weakest extractants (the single extractions with dilute $NaNO_3$ and pure H_2O) in the acidic tailings, indicating that potentially, these metals may leach into receiving waters. However, under the natural site conditions with low rainfall and high potential evapotranspiration, drainage into groundwater is negligible. Exceptional cases would occur during the typical strong rainstorms in spring and autumn where preferential flow may cause drainage to ground and surface waters.

The work shows that the results from extraction procedures should be carefully interpreted, especially regarding the most soluble fractions in soil, because the choice of an extractant may compromise subsequent conclusions and therefore lead to an incorrect risk assessment. In materials such as mine tailings with high concentrations of soluble metal(loid)s, the choice of the extractant is therefore critical for accurate risk assessment.

Future research could focus on immobilising the metal(loid)s in these sites to prevent ground- and surface waters contamination.

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