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Bioaccessibility of Cd and Pb in Tailings from a Zinc Smelting in Brazil: Implications for Human Health

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Abstract

Soils and wastes enriched with heavy metals may present significant ecological and human health risks. A considerable number of mining/smelting areas exist in Brazil, where high levels of metals have been found, as well as in their surrounding soils and sediments. However, studies of bioaccessibility of metals in soils/tailings from these areas are scarce, despite their potential informational contribution concerning exposure risks for residents near these areas. This study evaluated tailing samples collected from four sites of a smelting area aiming to: (i) evaluate the presence of metals of potential concern; (ii) investigate Cd and Pb bioaccessibility; and, (iii) determine the desorption kinetics of Cd and Pb. Five composite samples were collected from each site, at two depths, from a zinc smelting area located near Três Marias city - MG, Brazil. Availability of Cd and Pb was measured using a bioaccessibility test and a desorption experiment. High concentrations of total Cd and Pb and great variability were found in the tailings (up to 1743 mg Cd kg⁻¹ and 8675 mg Pb kg⁻¹), indicating the importance of adequate planning for their final disposal, in order to avoid contamination in the surrounding environment. Cadmium and Pb bioaccessibility percentages in the intestinal phase were less than 47 and 4%, respectively, which represents significant fractions not available for absorption in the intestinal tract. However, this material has to be monitored since its bioaccessibility may increase with eventual physicochemical changes, releasing Cd and Pb. Desorption kinetics experiments revealed that the Pb in the samples remained in less

labile fractions whereas Cd was found in more labile fractions, which is in accordance with the bioaccessibility result.

Keywords: trace elements; anthropogenic impacts; in vitro test; environmental contamination.

Introduction

Mining and smelting of metals are important economic activities since they contribute to the income of the country and generate employment, besides producing a range of different metals that can have countless uses in various contexts. Yet, mining and smelting activities have resulted in the generation of large quantities of wastes, which can be a relevant source of environmental contamination by trace elements (Alloway, 1990), such as cadmium (Cd), lead (Pb), and zinc (Zn). These metals may be transferred to the water, soils, plants and other environmental compartments, and eventually enter the human bodies through food chains or direct ingestion, representing a considerable threat to human health (Bi et al., 2006).

Trace elements such as Cd and Pb have been investigated in several compartments (e.g. water, plants, food, soil dust, agricultural soil, wastes) due to their potential toxic effects on humans and animals. Lead and Cd are ranked numbers two and seven, respectively, in the priority list of 275 hazardous substances to human health by ATSDR (2011). Human exposure to Cd can result in kidney dysfunction, skeletal disorders (i.e., Itai-Itai disease), and respiratory problems (Jarup, 2003). Lead poisoning can cause serious reactions in the infant human body, affecting children's nervous system and reducing their intelligence (Han et al., 2012).

There are a significant number of mining/smelting areas of metals in Brazil, especially in the state of Minas Gerais, and relatively high concentrations of trace elements have been found in the wastes from these areas and in their surrounding soils and sediments (Dias-Júnior et al., 1998; Ribeiro-Filho et al., 1999; Matschullat et al., 2000; Bundschuh et al., 2012). According to Carrizales et al. (2006), metal concentration in soils from urban areas located in the vicinity of mine/smelter sites is higher than background levels. Total metals content analysis (e.g. acid digestion) has been used in the characterization of contaminated soils/wastes by trace elements in order to address human health risk. However, the total concentration of elements does not reflect the proportion that might be available to humans and other forms of life (Demetriades et al., 2010). Thus, bioaccessibility tests such as IVG (Rodriguez et al., 1999) and PBET (Ruby et al., 1996), among others, have been suggested in order to

obtain a more realistic health risk assessment. Ruby et al. (1996, 1999) define the term bioaccessibility, regarding human exposure by soil ingestion, as the fraction of a potential toxicant in soil/wastes that becomes soluble in the gastrointestinal tract and is then available for absorption. If this fraction crosses a biological membrane it is then bioavailable. Bioavailability is considered a tool for better decision making regarding risk assessments and remediation purposes (Harmsen and Naidu, 2013). Inaccurate risk assessments for human health or for ecological purposes often result in an unnecessary clean-up of 'contaminated' sites and, consequently, a substantial and needless cost for the industries and the government (Lamb et al., 2009).

Incidental ingestion of soils/tailings particles via hand-to-mouth contact by children is a highly significant pathway of direct heavy metal exposure contributing to human health risk (Rodriguez et al., 1999; Hemond and Solo-Gabriele, 2004; Kwon et al., 2004). Based on studies of soil ingestion by children, guideline values were set by the USEPA (2002), at a mean of 100 mg day⁻¹ for children between 1 and 6 years old. For metals that are strongly adsorbed to soil particles, this route of exposure might be the most relevant form of human contamination. Therefore, we point out the relevance of characterization studies, especially bioaccessibility analyses and metal desorption experiments of tailings from mining/smelting areas located in urban surroundings. Such studies are scarce in Brazil and may give relevant information on the risk from exposure of residents living around these areas.

Tailing samples collected from four sites of a smelting area were used in this study with the aim of: (i) assessing the presence of metals of potential concern; (ii) investigating the bioaccessibility of Cd and Pb, and (iii) determining the desorption kinetics of Cd and Pb from such tailings. The study area is a zinc smelting area located very close to Três Marias city - MG, Brazil, and to the São Francisco River, which is one of the most important Brazilian rivers.

Materials and Methods

Site description and sampling

The smelter tailing samples selected for this study were collected at the facilities of a zinc smelting area located in Três Marias, in the Northwest of Minas Gerais - Brazil, from four sites, as follows: Eu, EB, pH9 and Tailings. Eu and EB represent experimental areas of a revegetation project (conducted in 2001-2002) where constant long-term Zn smelting activities in the past left a significant contaminated tailing deposit. In both areas, *Eucalyptus camaldulensis* was planted with a 2-m spacing between the plants and a mixture of non-contaminated soil, limestone, organic residue and fertilizer (N-P-K) was

placed into the planting holes. In the EB area, a 2-cm limestone layer and then a 20-cm non-contaminated soil layer were applied in between the rows of eucalyptus and at last *Brachiaria decumbens* was seeded. The pH9 site comprehends an inactive area of waste deposits with alkaline characteristics. When the samples were collected the area had several plant species of Cerrado vegetation. “Tailings” hereafter is used to describe an area (pond) used for waste depositions from the Zn smelting.

Five composite samples were randomly collected from each site at two depths (0-2 and 2-10 cm), using a stainless steel straight blade. Each composite sample consisted of five sub-samples from a 4-m² area. The samples were transported to the Soil Science Department at the Federal University of Lavras, Brazil, air-dried and sieved to less than 2 mm.

Basic chemical characterization

Two composite samples from each site (one at 0-2 cm and the other at 2-10 cm) were selected in order to perform chemical characterization analysis. The concentration of the elements in the samples (disaggregated and sieved to <250 µm fraction) was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after microwave-assisted acid digestion by the EPA method 3051. The organic matter (OM) content in the tailings (<2 mm) was measured following the Walkley-Black methodology (Nelson and Sommers, 1996).

Procedure for total Cd and Pb extraction

Total (or pseudototal) Cd and Pb contents in the smelter tailing samples were carried out using microwave-assisted acid digestion of the samples by the EPA method 3051A. For this procedure, 0.5 g of the samples (only sieved to <250 µm fraction) was transferred to microwave vessels filled with 5 mL of concentrated HNO₃. After digestion, the extract was filtered and diluted with ultrapure water (5 mL). The filtered extracts were preserved under refrigeration (4°C) until quantification using either graphite furnace atomic absorption spectroscopy (GFAAS) or flame atomic absorption spectroscopy (FAAS) on a Perkin Elmer AAnalyst 800 equipment.

Bioaccessibility of Cd and Pb

An in vitro Physiologically Based Extraction Test (PBET) protocol – a simulation of sequential digestion in the stomach and intestine proposed by Ruby et al. (1996) – was performed to determine the

contents of bioaccessible Cd and Pb in the smelter tailing samples. The gastric phase consisted of a mixture of 1 g of air-dried tailings (only sieved to <250 µm fraction – particles very likely to adhere to the hands of children and be eventually ingested (Maddaloni et al., 1998)) with 100 mL of a gastric solution that was prepared using 1 L of ultrapure water, 1.25 g of pepsin (Sigma-Aldrich, Cat. No. P7000), 0.5 g of citrate (Sigma-Aldrich), 0.5 g of malate (Sigma-Aldrich), 420 µL of lactic acid (syrup – 85% w/w, Sigma-Aldrich) and 500 µL of acetic acid (>99.7%, Sigma-Aldrich). The gastric solution was acidified before adding the samples with concentrated HCl (37%, Merck) to reach pH = 2.50±0.05. The Erlenmeyer flasks containing the gastric solution and the solid material were placed in a water bath at 37±0.5°C and left under constant horizontal shaking (100±2 rpm) for 1 hour.

The intestinal medium consisted in adjusting the gastric solution pH with saturated NaHCO₃ (pa, Merck) solution to 7.0±0.1 and then adding 175 mg of bile salts (Sigma-Aldrich, Cat N° B8631) and 50 mg of pancreatin (Sigma-Aldrich, Cat N° P1500). The container with the mixture was also left under horizontal shaking (100±2 rpm) for 2 hours at 37±0.5°C. At the end of each phase (gastric and intestinal), 5 mL were collected and centrifuged at 10,000 rpm for 10 min and the supernatant was filtered through a membrane filter of 0.45 µm pore size. The extracts were preserved under refrigeration (4°C) until analysis by GFAAS or FAAS.

The percentages of bioaccessible Cd and Pb were calculated using the following equation:

$$\text{Bioaccessible metal (\%)} = \frac{\text{In vitro metal}}{\text{Total metal}} \times 100$$

Desorption kinetics experiments

Cadmium and Pb release kinetics experiments in the smelter tailing samples were performed using a stirred-flow technique, which lessens diffusion effects and re-adsorption phenomena through the constant mixing in the reaction chamber, and removal of the metals in the effluent solutions (Sparks, 2003). Similarly to the experimental set up illustrated by Strawn and Sparks (2000), our experiments were carried out using two different desorptive solutions: (1) a 0.1 M CaCl₂ solution adjusted (with NaOH or HCl solutions) to the smelter tailings pH, and (2) a Mehlich-1 (0.05 M HCl + 0.0125 M H₂SO₄) solution. The desorbing solution passed through the chamber containing the solid sample at a constant flow by a pump. The chamber was covered with a 25-mm filter membrane of 0.45 µm pore size to separate the solids from the solution. The chamber volume of 12 mL contained a suspension of 0.6 g of sample (<250 µm, this being the same particle size used for total and bioaccessible analyses), which was stirred

at 400 rpm with a magnetic stir bar. The experiments were performed in duplicate, during 210 min at a flow rate of 0.9 mL min^{-1} , and the effluent was collected every 2 minutes for the first 10 min and every 10 min thereafter for a total of 210 min. Cadmium and Pb concentrations were analyzed using ICP-AES, to subsequently calculate cumulative Cd and Pb desorption percentages, in accord with Shi (2006).

Quality assurance and quality control

All reagents used in this work were analytical grade. Ultrapure water with a resistivity of $18.2 \text{ M}\Omega\text{-cm}$ was used to prepare all solutions. Glassware, flasks and materials were treated with a 10% HNO_3 solution for 24 hours, and rinsed three times with distilled water before use. All chemical analyses were performed in triplicate, except for the desorption experiment, which was carried out in duplicate, with blank samples conducted in parallel for quality control purposes. Certified reference materials (BCR 143R, NIST 2710 and NIST 2710a) were used to evaluate the reproducibility and the accuracy/precision of the tested analytical procedures. Recovery percentages of trace elements in the samples showed a reliable analytical data accuracy for the analyses of total contents. The percentages of bioaccessible Cd (78% - gastric and 44% - intestinal) and Pb (25% - gastric and 12% - intestinal) found in the certified material NIST 2710 were in good agreement with the indicative values found in other studies. Hamel et al. (1998) reported the bioaccessibility of Cd and Pb for NIST 2710 as $51.4 \pm 18.5\%$ and $36 \pm 14\%$, respectively, at a liquid-to-solution ratio of 100:1 in the gastric phase. Rodriguez et al. (1999) found Pb bioaccessibility in the gastric phase (with dough) of 28%. Ellickson et al. (2001) reported bioaccessibility of Pb in the intestinal step as 10.7%. Cadmium bioaccessibility values found for the NIST 2710a and BCR 143R were 33% (gastric), 33% (intestinal) and 46% (gastric), 38% (intestinal), respectively. For Pb, the values were 33% (gastric), 3% (intestinal) and 1% (gastric), 1% (intestinal), respectively. To the best of the authors' knowledge, no previous research has indicated the bioaccessibility values for these standards that could be used as a reference for us to compare the results from this study.

Results and Discussion

Chemical characteristics of the smelter tailings

Smelter tailing samples from the studied sites showed intermediate values of pH (Table 1). The highest pH value found was for the pH9 site due to the alkaline conditions of the wastes disposal in this area. The OM contents in the samples were low, ranging from 0.5 to 1.5%, with the highest values – 1.5

and 1.3% – for the EB and the pH9 sites, respectively. This occurred because of the existence of plants in these areas, the pH9 site being naturally covered with plants of Cerrado vegetation and EB the area where the revegetation project took place. Comparing the revegetation sites (Eu and EB), the content of the surface OM (0-2 cm) and the pH of the EB site were higher than the values found in Eu. This difference is a result of the surface application of limestone and the growth of brachiaria in between the rows of eucalyptus in EB. The Eu site had no plant species in between the rows.

Concentrations of trace elements in the smelter tailings determined in this study were compared with the industrial investigation threshold established by Conama (2009), since there are no guideline values for trace elements in tailings in the Brazilian legislation until the present date. The threshold values (in mg kg^{-1}) are: As (150), Cd (20), Cr (400), Cu (600), Pb (900), and Zn (2000). The samples showed levels of As and Cr well below these values (Table 1). The Eu site had Cd contents above the threshold, as well as EB (0-2 cm depth), which also showed high levels of Zn. The pH9 sample was the only one that presented low levels of trace elements, which was expected since this area had several species of plants growing normally. Therefore, this site is considered to be non-contaminated by trace elements – taking into consideration the industrial investigation threshold. On the other hand, Tailings is the most contaminated site, with the highest levels of Cd (621 mg kg^{-1}), Cu (2518 mg kg^{-1}), Pb (7431 mg kg^{-1}), and Zn ($45,058 \text{ mg kg}^{-1}$). Studies carried out by Lamb et al. (2009) showed very high concentrations of Cd, Cu, Pb, and Zn in contaminated soils from Australia – up to $302 \text{ mg Cd kg}^{-1}$, $6841 \text{ mg Cu kg}^{-1}$, $12,000 \text{ mg Pb kg}^{-1}$, and $39,000 \text{ mg Zn kg}^{-1}$. The authors reported that, despite the high total metal concentration of the contaminated soil, Zn, Cd, and Pb were not generally found at elevated levels in the pore-water. A previous study on geochemical position of metals in soils near a mine/smelter in Poland reported the highest concentrations of Cd, Pb, and Zn in a forest soil – 200 mg kg^{-1} , $25,000 \text{ mg kg}^{-1}$ and $20,000 \text{ mg kg}^{-1}$, respectively (Chrastný et al., 2012).

Considering their importance in terms of human health effects, for the present study we selected the trace elements Cd and Pb for investigation of total and bioaccessible contents in all samples collected (five samples from each site at two depths) and of desorption kinetic in one sample from each site at the 0-2 cm depth.

Table 1. Chemical characteristics of the smelter tailings from a zinc smelting area

Samples	pH	OM	As	Ca	Cd	Cr	Cu	K	Mn	P	Pb	S	Zn	Al	Fe
	(H ₂ O)	(%)						mg kg ⁻¹						(%)	
Eu ¹	5.1	1.0	2	172	52	25	19	340	55	95	23	340	819	1.2	2.0
Eu ²	4.8	0.8	2	144	39	18	27	266	81	57	45	309	1104	1.1	1.8
EB ¹	6.1	1.5	3	1438	30	35	58	896	800	230	157	657	3301	2.5	4.1
EB ²	6.3	1.2	8	564	11	22	77	507	1108	184	293	468	3268	1.1	3.5
pH9 ¹	6.5	1.3	2	994	15	64	29	661	452	190	46	3261	954	0.6	3.1
pH9 ²	6.7	0.9	1	421	6	23	27	1020	134	179	26	2085	403	0.7	3.0
Tailings ¹	5.5	0.6	59	48521	621	2	2518	1647	29169	147	7431	66200	45058	0.3	2.5
Tailings ²	5.0	0.5	36	25678	525	14	561	711	9044	223	3455	40843	25321	0.4	2.8
NIST 2710 ³	Recovery (%)		90	Dm	99	Nc	94	29	92	86	92	83	88	36	86
BCR 143R ³			Nc	Nc	97	105	98	Nc	103	Nc	97	Nc	89	Nc	Nc

^{1,2}Collected at the depths of 0-2 and 2-10 cm, respectively; ³Certified reference material

OM determined by the Walkley-Black method; EPA method 3051 – ICP analyses

Dm = analyzed by different methods; Nc = noncertified value

Industrial threshold (mg kg⁻¹) for As (150), Cd (20), Cr (400), Cu (600), Pb (900) and Zn (2000) established by Conama (2009)

Total Cd and Pb contents

The samples showed a great variability in the contents of Cd and Pb not only among the different sites, but also in replicate samples from the same site and from the same sampling depth, with average values ranging from 6 up to 773 mg kg⁻¹ for Cd and from 32 up to 6256 mg kg⁻¹ for Pb (Figure 1). The Tailings site showed extremely high concentrations of the elements – up to 1743 mg kg⁻¹ for Cd and 8675 mg kg⁻¹ for Pb. Such heterogeneity in trace elements contents in samples of the same area is common in tailings from smelting areas due to constant waste disposals with varied contamination levels. Various studies have reported great variability in metal concentrations among different sites. Rieuwerts and Farago (1996) reported contents of Cd ranging from 0.1 to 48 mg kg⁻¹ and of Pb ranging from 55 to 37,300 mg kg⁻¹ in soils from the vicinity of a mining and smelting area in the Czech Republic. The levels of metals decreased with increasing distance from the smelter, i.e., the higher the distance from the smelter, the lower the levels of metals. Studies carried out by Bi et al. (2006) in samples from Zn smelting areas in China revealed that the soil from the cornfield near the smelting sites had elevated concentrations

of Cd (5.8 to 74 mg kg⁻¹), Pb (60 to 14,000 mg kg⁻¹), and Zn (260 to 16,000 mg kg⁻¹). High concentrations of heavy metals were also found in corn plants and in the moss samples from the smelting sites.

For the interpretation of the contents found in this study, the values established by Conama (2009) for Cd and Pb were once again considered. For Cd, most of the sites had values above 20 mg kg⁻¹, except for pH9 (Figure 1). The Tailings sample stood out for having presented mean content approximately 38 times higher than the industrial threshold. It also exceeded the limit for Pb, with average content approximately 7 times greater. The other sites showed Pb concentration well below the threshold.

Contamination by multiple metals (such as Pb, Zn, Cd, Cu, and Ni, that can co-occur in mineral deposits) is rather common in the surroundings of mining/smelting areas, with substantial variation of the bioavailable levels among the sites (Schneider et al., 2007). However, total concentration of trace elements in soils/tailings does not usually provide enough information to determine the element bioavailability and mobility. Metals in soils/tailings are related with certain physicochemical parameters that control the availability of metals in the environment (Anju and Banerjee, 2011).

No pattern was noticed in the contents of Cd and Pb among the stratified samples (0-2 and 2-10 cm) (Figure 1). For a risk assessment considering involuntary ingestion of soils/tailings by children (i.e. hand-to-mouth activity), the most important layer of soil to be considered is the most superficial one (the first centimeters). However, it is relevant to have samples collected from different stratifications in a risk assessment because the particles on the top layer of the soil/tailing can be eroded by wind and water (rain and surface run off) and transported to urban areas, rivers, farmland, etc, causing the layer underneath to become the top layer (Ono et al., 2012).

Figure 1. Box plot of total Cd and Pb contents in tailings from a zinc smelting area. Each box represents the lower and upper quartiles, and the band within the box represents the median Cd and Pb values. Whiskers represent minimum and maximum values for data and the dot represents the mean value. For each site, the right and left boxes represent the depths of 0-2 and 2-10 cm, respectively. Industrial threshold = soil guideline value for industrial areas established by Conama (2009). Recovery (%) of the certified materials: Nist2710 (Cd: 84; Pb: 83), Nist2710a (Cd: 119; Pb: 103), BCR143R (Cd: 99; Pb: 81).

Bioaccessibility of Cd and Pb

Similarly to the total content, a great variability was noticed in the concentration of bioaccessible Cd and Pb both among and within the sites, with the Tailings site showing the highest contents (Figures 2 and 3). The mean contents of bioaccessible Cd in the Eu and in the Tailings sites for both depths were above the industrial threshold (Figure 2). In addition, very high Cd contents (up to 807 mg kg⁻¹) were observed for the Tailings site at the 2-10 cm depth, this value being 40 times higher than the industrial threshold.

Figure 2. Box plot of bioaccessible Cd content in tailings from a zinc smelting area. Each box represents the lower and upper quartiles, and the band within the box represents the median Cd value. Whiskers represent minimum and maximum values for data and the dot represents the mean value. For each site, the left and right boxes represent the gastric and intestinal phases, respectively. Industrial threshold = soil guideline value for industrial areas established by Conama (2009).

The bioaccessible Pb contents were well below the industrial threshold in all sites at both depths (Figure 3), which confirms the necessity of not taking into consideration only the total content of the element when assessing human health risks, since the results can be overestimated. Several studies have indicated that the bioaccessibility of a contaminant is well less than 100%, and have therefore suggested the use of bioaccessible contents instead of total contents when assessing health risk, due to their greater accuracy (Ruby et al., 1996; Hamel et al., 1998; Rodriguez et al., 1999; Turner and Ip, 2007; Girouard and Zagury, 2009; Juhasz et al., 2010; Lu et al., 2011; Ono et al., 2012; Toujaguez et al., 2013). No pattern was observed in the contents of bioaccessible Cd and Pb (Figures 2 and 3) among the stratified samples (0-2 and 2-10 cm), showing a similar behavior to that found for total contents (Figure 1).

Figure 3. Box plot of bioaccessible Pb content in tailings from a zinc smelting area. Each box represents the lower and upper quartiles, and the band within the box represents the median Pb value. Whiskers represent minimum and maximum values for data and the dot represents the mean value. For each site, the left and right boxes represent the gastric and intestinal phases, respectively.

Percentages of bioaccessible Cd and Pb

The percentages of bioaccessible Cd and Pb for each area and depth were calculated as the ratio between the average content (mg kg^{-1}) of bioaccessible metal and total metal (Figure 4). The pH9 site showed a high percentage of bioaccessible Cd in the gastric phase at both sampling depths (75 and 67%, at 0-2 and 2-10 cm, respectively) (Figure 4). Despite that, its bioaccessible contents (Figure 2), as well as the total (Figure 1), were below the industrial threshold, being thus considered a non-contaminated area. The other sites presented moderate bioaccessible Cd (%) in the gastric phase, ranging from 32 to 44% (Figure 4). The Eu site, besides having presented bioaccessible and total Cd contents (Figures 1 and 2) above the industrial threshold, showed the highest bioaccessible Cd (%) in the intestinal phase (Figure 4) for both depths (47 e 43%, at 0-2 and 2-10 cm, respectively).

The Tailings site showed one of the lowest percentages of bioaccessible Cd and the lowest percentage of bioaccessible Pb (<3%) (Figure 4), even though it showed the highest contents of total and bioaccessible Cd (Figures 1 and 2) – above the industrial threshold – and total and bioaccessible Pb (up to 8675 and 215 mg kg^{-1} , respectively) (Figures 1 and 3), the latter being below the industrial threshold. However, there is still a need to monitor this material because a range of physicochemical changes may occur over time, increasing the bioaccessibility and generating Cd and Pb release to the environment. A

study on bioavailability of Cd, Pb, and As in an abandoned mine site in Spain indicated that pH and mineralogical composition were important factors controlling metal bioavailability in the materials (Navarro et al., 2006). Another study reported that the bioaccessibility of Cd, Pb, and Zn in smelter-contaminated agricultural soils from France was affected by various physicochemical parameters, such as sand, carbonates, organic matter, assimilated P, free Al oxides, and total Fe contents (Pelfrène et al., 2011a).

Mean bioaccessible Cd and Pb (%) were higher in the gastric phase when compared to the intestinal phase (except for Cd in the Eu site), the difference between the two phases being higher for Pb (Figure 4). This indicated that most of the Cd and the Pb was dissolved in the stomach and after that a portion remained soluble in the intestine, being potentially available for absorption. This result is relevant since the absorption of metals occurs mainly in the intestines and insignificantly in the stomach (Charman et al., 1997; Daugherty and Mrsny, 1999). Similarly, Lu et al. (2011) pointed out that the bioaccessibility of Pb in the gastric phase (39.1%) was much greater than in the intestinal (6.9%) in soils from different land uses (urban parks, roadsides, industrial sites and residential areas) in China, and attributed this to the reduced solubility of Pb at a much higher pH in the intestinal phase than in the gastric. The dissolution of Pb in the acidic gastric phase is strongly dependent on pH, i.e., its solubility decreases significantly (by 65%) with increasing of the gastric pH from 1.3 to 2.5 (Ruby et al., 1996). Also, it was reported that the adsorption of Cd in the soil increased rapidly with increasing solution pH within the range of 2 to 5 (Naidu et al., 1994).

However, the highest percentages of bioaccessible metals do not necessarily occur in the gastric phase. A previous study on bioaccessibility of metals in dust from several domestic and working settings reported that, compared to the accessibility in the stomach, the accessibility in the more alkaline carbonate-rich intestine was either lower (Al, Ca, Cd, Mn, Ni, Sn, Pb, Zn), similar (Co, Cu, Fe) or greater (Cr, U) (Turner and Ip, 2007). The authors attributed these observations to precipitation and/or readsorption in the intestine, stabilization by complexation, or anion-like adsorption of negatively charged polyatomic species, respectively. Several studies indicate that Cd and Pb bioaccessibility is greater in gastric phase extracts when compared to intestinal (Carrizales et al., 2006; Tang et al., 2006; Turner and Ip, 2007; Juhasz et al., 2010; Lu et al., 2011; Pelfrène et al., 2011b).

Figure 4. Percentage of bioaccessible Cd and Pb in tailings from a zinc smelting area and in a certified reference material.

Percentages of bioaccessible Cd were much higher than the bioaccessible Pb values, especially in the intestinal phase (Figure 4), indicating that Cd occurs in more labile forms than Pb. Navarro et al. (2006) reported that in a mine site Cd was the most bioavailable metal in both the stomach and the intestinal phases (47 and 27.8%, respectively), followed by Pb (25.3 and 11.5%). In smelter-contaminated agricultural soils, Pelfrène et al. (2011a) found a mean bioaccessibility (%) in the gastric and intestinal phases of 82 and 45% for Cd, and 55 and 20% for Pb, respectively, indicating that Cd was mainly found in more available fractions and Pb was mostly present as adsorbed or occluded by Fe/Mn oxides. Several studies have shown bioaccessible values higher for Cd than for Pb in soils, urban dust, and mine tailings (Turner and Ip, 2007; Pelfrène et al., 2011a; Okorie et al., 2012).

Some studies have investigated the effects of amendments in the reduction of the availability of metals in contaminated soils/tailings. The addition of P-containing amendments (P fertilizers) was found to effectively reduce the bioaccessibility of Pb in contaminated soils (Tang et al., 2004). In general, the effectiveness of the treatments in the intestinal phase was, in decreasing order: hydroxyapatite, phosphate rock, hydroxyapatite plus single super-phosphate, single super-phosphate. In a study on Pb toxicity reduction in a highly contaminated military shooting range soil in Korea, Ahmad et al. (2012) found that, compared to the unamended soil, the bioavailability and bioaccessibility of Pb decreased by 92.5% and 48.5% with mussel shell, by 84.8% and 34.5% with cow bone, and by 75.8% and 12.5% with biochar, respectively.

Desorption kinetics experiments

In order to assess the exchangeable metal fraction and the phytoavailable metal (or not stable at lower pH – relevant in the presence of acid rain or near the roots of plants) fraction, stirred-flow desorption experiments were conducted using a 0.1 M CaCl_2 (adjusted to the samples pH) or a Mehlich-1 (pH = 1.6 ± 0.1) solution. The small sample chamber, the relatively low solid:solution ratio and the constant flow rate ensured that none of the desorption products would be re-adsorbed onto the solid sample (Sparks, 2003). To compare the desorption behavior of smelter tailings, the amount of metal released was plotted as the cumulative metal desorption (% of total concentrations) as a function of time (Figure 5).

The experimental data indicated an initially rapid desorption of Cd by both extraction solutions (CaCl_2 and Mehlich-1) in the first 30 minutes (Figure 5). After that, small quantities of Cd were released until the end of the experiment (210 min), when equilibrium was reached. At the completion of the 210 min dissolution experiment, Cd desorption was over 94% for Eu, 71% for EB, 42% for pH9 and 71% for Tailings. The CaCl_2 solution desorbed a slightly lower amount of Cd from the samples than the Mehlich-1, except for the Tailings sample. This result shows that most of the Cd present in the samples was in the labile forms (exchangeable).

The percentage of Pb released by CaCl_2 was of 49% and 19% for Eu and Tailings samples, respectively, whereas by Mehlich-1 it was found to be 62% and 31% for the same samples, during the 210-min experiment (Figure 5). For the EB and pH9 samples, however, percentages of Pb were very low

(1 and 1.5%, respectively) when desorbed by CaCl_2 and high (73 and 46%, respectively) when desorbed by Mehlich-1.

Lead desorption by the Mehlich-1 solution did not reach the equilibrium during the dissolution experiment, indicating that more of this element would have been released after 210 min. The percentage of Pb removed from the Tailings sample by both solutions tended to be linear (increased rapidly) during the 210 min and did not reach equilibrium. In general, this study showed that the exchangeable Pb fraction was not predominant in the samples. The greatest Pb release occurred in the extraction solution with lowest pH, indicating that the Pb fractions appeared in more recalcitrant forms in the samples. The fact that Cd appeared in the more labile forms (exchangeable) and Pb in the more recalcitrant forms (less labile) is in agreement with the results of bioaccessibility (Figure 4), in which Cd showed to be more bioaccessible and Pb less bioaccessible.

Figure 5. Percentage of Cd and Pb release from smelter tailing samples during a stirred-flow dissolution experiment using a 0.1 M CaCl_2 solution adjusted to the smelter tailings pH and a Mehlich-1 solution.

Conclusions

The smelter tailing samples from the Zn smelting area, especially from the Tailings site, have high concentrations of Cd, Cu, Pb and Zn. More detailed analyses revealed that Cd and Pb concentrations were considerably elevated in the Tailings site and highly variable among and within the sites. Thus, we point out that the final disposal of these materials requires adequate planning, in order to avoid Cd and Pb contamination of the surrounding environment. Even though the study detected elevated levels of Cd and Pb, it has to be taken into consideration the fact that the population does not have free access to the sites studied, which results in a rather low risk of exposure.

The bioaccessibility of Cd and Pb in the intestinal phase (less than 47 and 4%, respectively) was less than half the total concentration of the metals. This indicates that a considerably high fraction of the elements was not available for absorption in the intestinal compartment (where the absorption takes place). Desorption kinetics experiments revealed that the Pb fraction in the samples was less labile (more recalcitrant) and the Cd fraction more labile (i.e. exchangeable fraction). This finding is in accordance with the bioaccessibility results.

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