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Environmental and health risk assessment of Pb, Zn, As and Sb in soccer field soils and sediments from mine tailings: solid speciation and bioaccessibility

Grégoire Pascaud · Thibaut Leveque ·
Marilyne Soubrand · Salma Boussen ·
Emmanuel Joussein · Camille Dumat

Abstract Areas polluted by the persistent presence of metal(loid)s induce health problems, especially when recreational activities (on land or water) promote human exposure to the pollutants. This study focuses on one of the most encountered worldwide mining waste, i.e. those from the extraction of Pb–Zn–Ag. The representative Pb–Zn-rich tailing (about 64, 100 m³) sampled is located near a soccer field and a famous river for fishing. The scientific interests is relative to: (1) mobility and bioaccessibility of metal(oid)s, (2) human risk assessments and (3) relationship between human risks and solid-bearing phases in the environment. Soccer field soils, tailings and sediments from the nearby river were sampled; moreover, metal(loid) speciation (from BCR experiments) and bioaccessibility were measured and solid speciation performed by X-ray diffraction and electron microscopy in order

to highlight metal(loid) dispersion and impact. Results demonstrate that the soccer field is highly contaminated by Pb, Zn, As and Sb due primarily to waste runoff. In terms of risk assessment, Pb and As human bioaccessibility highlights the major health risk (48 and 22.5 % of human bioaccessibility, respectively). Since local populations are regularly in close contact with metal(loid)s, the health risk due to pollutant exposure needs to be reduced through sustainable waste disposal and the rehabilitation of polluted sites.

Keywords Bioaccessibility · Mineralogy · BCR · Soccer field · Metals · Metalloids

Introduction

The major anthropogenic sources of metal(loid)s in the environment are mining and smelting activities (Uzu et al. 2009). One of the main concerns regarding mining activities is the production of a huge amount of wastes, typically stored in the vicinity of mines (Sobanska et al. 2010). Since these industrial waste materials contain inorganic pollutants, they represent secondary sources of pollution for soils, water and the atmosphere. Moreover, these wastes can induce health-related consequences through direct particle ingestion or inhalation (Uzu et al. 2011) or food chain impacts (Schreck et al. 2012). It has therefore become necessary to assess the behavior and impact of these process wastes in sensitive sanitary contexts like playgrounds in relation to their potential mobility towards the environment (Gieré et al. 2003). It has been well established that the chemical speciation of metal(loid)s can strongly influence both their behavior in soils and (eco)toxicity as regards their solubility, mobility and bioavailability (Schreck et al. 2011).

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Over the past decade, a number of studies have been performed for the purpose of determining the general behavior of heavy metals in various soil contexts, such as acidic (Birkefeld et al. 2006; Chen et al. 2006) or alkaline, as well as in a carbonated context (Fotovat and Naidu 1998; Boussen et al. 2013). From a classical perspective, the behavior of chemical elements is assessed by a sequential or selective extraction procedure like BCR method, which provides semi-quantitative information on their compartmentalization in soils and their mobility and bioavailability in relation to the stability of interactions developed with soil components or the solid metal compounds formed (e.g. Van Herreweghe et al. 2003; Neel et al. 2007; Pueyo et al. 2008; Anju and Banerjee 2010; Smith et al. 2011; Uzu et al. 2011; Boussen et al. 2013). The coupling of this BCR chemical procedure with a mineralogical approach (e.g. XRD, SEM, TEM) allows determining the various bearing phases of metal(loid)s in soils (Kovács et al. 2006; Otones and Alvarez-Ayuso 2011; Chiang et al. 2010) and then leads to predicting their stability.

According to Pelfrène et al. (2012), soils enriched with metal(loid)s can pose a potential threat to human health if directly ingested or transferred through food. However, the conventional BCR extraction procedure is not suitable for assessing the bioavailable fraction of pollutants in the case of accidental soil ingestion (e.g. children through outdoor hand-to-mouth activities) (Day et al. 1979; Duggan et al. 1985; Wixson and Davies 1994). In reality, the human bioavailability of a pollutant, whose contaminant fraction is absorbed through the gastrointestinal tract and reaches systemic circulation (Semple et al. 2004; Denys et al. 2009), is firstly controlled by its release from the solid soil phase into the stomach, which defines bioaccessibility. Recently, the Bioaccessibility Research Group of Europe (BARGE) has developed a standardized procedure (Cave et al. 2006) (known as the Unified Bioaccessibility Method, or UBM) for current use in contaminated soil studies (Denys et al. 2009; Broadway et al. 2010; Button et al. 2008; Caboche et al. 2010; Denys et al. 2007; Pelfrène et al. 2011; Pelfrène et al. 2012).

The main objectives of this survey are to estimate the potential environmental and health risks associated with Pb, Zn, As and Sb near the contamination source (an abandoned mine tailing) relative to both receptor soils, i.e. a soccer field and sediments. The scientific impact and interests of this study pertain to the: (1) mobility and bioaccessibility of metal(oid)s, (2) human risk assessments and (3) relationship between human risks and solid-bearing phases in the environment. Compartmentation and speciation have been respectively determined by BCR sequential extraction and mineralogical characterization. Moreover, the bioaccessibility of Pb, Zn, As and Sb, in using both the gastric and intestinal phases,

has been measured in order to assess the human bioavailability of pollutants and highlight the health risks caused by these contaminants with regard to the actual recreational activities being practiced.

Materials and methods

Site description

This study focuses on a former Pb–Ag mine, located in the French Massif Central region, that has been abandoned since the early 1900s. Annual rainfall at the site roughly equals 983 mm, and the mean temperature is 9.5 °C. From 1860 to 1900, the Pontgibaud mine produced approximately 64, 100 m³ of mining waste enriched with contrasted metal(loid)s: Pb, Zn, Sb and As. The lack of vegetation combined with the tailing pile slopes has caused material instability. These mine tailings have been exposed to both hydraulic and wind erosion, inducing a dispersion of toxic mining wastes in the river and on the soccer field (Fig. 1). Moreover, these waste materials were used during the 1960s as the soccer field underlay, the pathway running along the site and the sand for concrete mixes. According to this, soccer field sampled is either classified as Technosols (‘dominated by human-made materials’) (FAO 2006). Recreational activities (land or water) have taken place at the site, serving to raise human exposure to the pollutants, particularly as regards soccer players and young children.

Sample collection and preparation

Various representative samples (up to 31) were extracted in order to expose the potential environmental risks from this tailing (references are indicated in Fig. 1). In sum, two composites (five-sample mixes) were drawn from the top of the tailing, referred to as T1 and T2. Sample T3 corresponds to the fines fraction of the waste material mobilized by runoff. The pathway (T4) and soccer field topsoil (soils 1a and 1b; 0–5 and 5–10 cm in depth respectively) were also sampled. Moreover, surface sediment (0–5 cm) in the river running below the tailing was sampled (Sed).

The samples were air-dried in the laboratory, then sieved to 2 mm and stored at ambient temperature in polyethylene containers.

Physicochemical analysis

The grain size fraction <63 µm was obtained after sieving. The soil pH was measured in a solid/liquid ratio of 1:5 with double deionized water (NF ISO 10390 Standard). The organic C content was determined by the loss ignition method. The cation exchange capacity (CEC) was determined according to

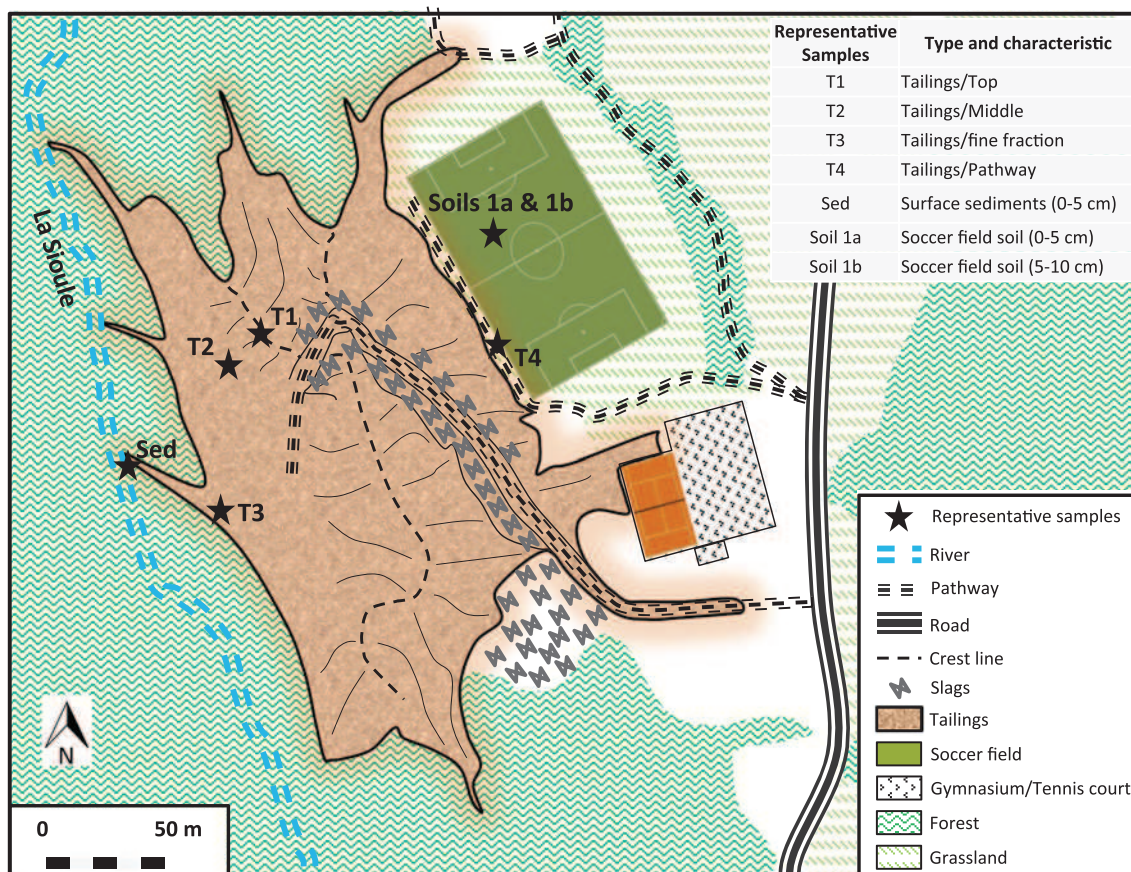


Fig. 1 Aerial photograph of the former mining area with sample localization

the 0.05 N cobaltihexamine method at the soil pH (NF ISO 31–130 Standard). Double deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used for all experiments. All reagents were of analytical reagent grade or higher purity.

Mineralogical analysis

Each sample was X-rayed after crushing by a PANalytical X'Pert Pro diffractometer equipped with a diffracted-beam monochromator. Analyses were carried out using Co K α radiation (40 kV, 40 mA) from 5 to 75 $^{\circ}2\theta$ with a step size of 0.04 $^{\circ}2\theta$ /s. The XRD patterns were interpreted by running the X'PertHighScore software. A semi-quantitative determination of the crystallized phases was performed according to the RIR method and has been reported in terms of sample representativeness.

Complementary scanning electron microscopy investigations were conducted on all samples after inclusion in resin and thinly polished. Samples were observed using a SEM Phillips XL30 operated at 20 KV and provided with an energy-dispersive X-ray spectrum (EDS) analyser. These samples had previously been Au–Pd coated.

Geochemical analysis

Chemical analyses

Total metal(loid) contents were derived from X-ray fluorescence analyses (XRF) using an XMET 5100 commercialized by OXFORD Instruments. Acquisitions were generated from pressed pellets at times varying from 60 to 180 s, for major or trace elements, respectively. The validation step involved total metal concentrations measured after acidic mineralization.

Sequential extractions

Sequential extractions were performed using the BCR protocol Pérez-Cid et al. (1998) as reported in Table 1. In sum, 1 g of materials was mixed with each solution. Following each step, supernatants were obtained after centrifuging at 3, 300 $\times g$, 15 min and filtration with a 0.45- μm filter reference. Metal(loid) contents were then analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on an IRIS Intrepid II XXDL apparatus. Duplicate analyses were performed on all samples.

Table 1 Sequential extraction protocol (BCR)

Fraction	Chemical reagents	Volume (ml)	Solid–solution ratio (g/ml)	Sonication time and power
F1: exchangeable fraction	Acetic acid (CH ₃ COOH) 0.11 mol/l	20	0.025	20 W for 7 min
F2: reducible fraction	Hydroxylammonium (HONH ₂ ·HCl) 0.10 mol/l (reagent brought back to pH 2 with nitric acid 69 %)	20	0.025	20 W for 7 min
F3: oxidisable fraction	Hydrogen peroxide (H ₂ O ₂) 30 %	10	0.05	20 W for 2 min
	Ammonium acetate (C ₂ H ₃ O ₂ NH ₄) 1 mol/l (reagent brought back to pH 2 with nitric acid 69 %)	25	0.02	20 W for 6 min

Bioaccessibility measurements

The bioaccessibility test simulates chemical conditions of the gastrointestinal tract and is used to reproduce the phenomena involved in the case of an accidental ingestion of polluted soil. This protocol is based on the BARGE-unified protocol (Denys et al. 2009; Pelfrène et al. 2012).

Several extracting solutions representing gastric and intestinal attacks were thus prepared (see Table 2). In sum, 0.6 g of soil were mixed in 9 ml of saliva (pH 6.5) and the mix was shaken for 5 min. Next, 13.5 ml of gastric solution were added (pH 1.0) and the pH suspension was adjusted to 1.2 using HCl acid at 37 % g g⁻¹. This suspension was then mixed with an ‘end-over’ agitator for 1 h at 37°C. pH remained between 1.2 and 1.7 by adding 37 % HCl. The intestinal phase was obtained after centrifuging 3,000×g for 5 min. Metal(loid) concentrations were derived after filtration (0.45 µm) by ICP-OES. This same protocol was then applied to an intestinal solution: 0.6 g of soil was mixed, with pH ranging between 5.8 and 6.8. Shaking lasted 4 h using an end-over agitator; centrifugation at 3,000×g took another 5 min. Sample solutions were analysed by ICP-OES on an IRIS Intrepid II XXDL

device. Bioaccessibility results were expressed in terms of percentage of total metal content. All tests were conducted in duplicate.

Results and discussion

Physicochemical parameters and total metal(loid) contents

The set of physicochemical parameters are listed in Table 3; pH values range from 3.9 to 6.3. On the whole, these low values are characteristic of the region's underlying acidic bedrock. The lowest pH values (3.9 to 4.3) are observed in the tailing samples (T1, T2, T3 and T4). Soil samples from the soccer field display a pH ranging from 6.0 to 6.3. The organic carbon contents of tailing and sediment samples were between 0.4 and 0.8 wt% and up to 7.7 wt% for topsoils. The cation exchange capacity (CEC) is similar for both the tailing and sediment samples (between 4.4 and 4.6 cmol kg⁻¹) and is highest for Soil 1a topsoil (12 cmol kg⁻¹) due to the presence of organic matter. Particle size analysis shows that sample T3 is rich in fine particles, as a result of the migration of fine particles from tailings by runoff

Table 2 Composition of the digestive solution used during the bioaccessibility test

Saliva	Gastric phase	Bile	Intestinal phase
KCl 89.6 g/l—10 ml	NaCl 175.3 g—15.7 ml	NaCl 175.3 g—30 ml	NaCl 175.3 g—40 ml
KSCN 20 g/l—10 ml	NaH ₂ PO ₄ 88.8 g/l—3 ml	NaHCO ₃ 84.7 g/l—68.3 ml	NaHCO ₃ 84.7 g/l—40 ml
NaH ₂ PO ₄ 88.8 g/l—10 ml	KCl 89.6 g/l—9.2 ml	KCl 89.6 g/l—4.2 ml	KH ₂ PO ₄ 8 g/l—10 ml
NaCl 175.3 g/l—1.7 ml	CaCl ₂ ·2H ₂ O 22.2 g/l—18 ml	HCl 37 % g/g—200 µl	KCl 89.6 g/l—6.3 ml
NaOH 40 g/l—1.8 ml	NH ₄ Cl 30.6 g/l—10 ml	urea 25 g/l—10 ml	MgCl ₂ 5 g/l—10 ml
urea 25 g/l—8 ml	HCl 37 % g/g—8.3 ml	CaCl ₂ ·2H ₂ O 22.2 g/l—10 ml	HCl 37 % g/g—180 µl
α-Amylase—145 mg	Glucose 65 g/l—10 ml	Bovine albumine—1 g	CaCl ₂ ·2H ₂ O 22.2 g/l—9 ml
Uric acid—15 mg	Glucuronic acid 2 g/l—10 ml	Porcine bile	Bovine albumine—1 g
Mucin—50 mg	Urea 25 g/l—3.4 ml		Pancreatin—3 g
	Glucosamine hydrochlorite 33 g/l—10 ml		Lipase—0.5 g
	Bovine albumine—1 g		
	Pepsin—1 g		
	Mucin—3 g		

Table 3 Physicochemical characteristics of the samples

Sample	<63 μm (g 100 g ⁻¹)	C org (g 100 g ⁻¹)	pH	CEC (cmol kg ⁻¹)	Pb (mg kg ⁻¹)	Zn	As	Sb
T1	25.3	0.6	4.3	4.5	16,603 $\pm$ 27	1,064 $\pm$ 7	354 $\pm$ 113	196 $\pm$ 14
T2	6.6	0.4	4.5	4.5	9,651 $\pm$ 19	786 $\pm$ 6	325 $\pm$ 72	157 $\pm$ 13
T3	79.5	0.4	3.9	4.4	38,412 $\pm$ 45	1,309 $\pm$ 9	330 $\pm$ 78	363 $\pm$ 18
T4	36.6	0.8	4.3	4.6	15,686 $\pm$ 222	1,177 $\pm$ 7	592 $\pm$ 111	228 $\pm$ 15
Sed	3.2	0.5	6.0	4.6	12,675 $\pm$ 23	652 $\pm$ 5	189 $\pm$ 55	195 $\pm$ 14
Soil1a	12.5	7.7	6.3	12.1	2,930 $\pm$ 106	995 $\pm$ 7	242 $\pm$ 54	159 $\pm$ 14
Soil1b	8.8	3.5	6.0	5.4	2,780 $\pm$ 104	949 $\pm$ 7	261 $\pm$ 53	167 $\pm$ 14
					DL=5	DL=3	DL=3	DL=34

DL detection limit

(hydric erosion). The physicochemical properties reveal similarities between the filling path materials (T4) and the tailings, with a slight enrichment in fine particles, which were probably also mobilized by tailing runoff.

In terms of metal(loid) contents, the tailing samples show relatively high values. Lead (Pb) contents are respectively 16,603 and 9,651 mg kg⁻¹ for T1 and T2 (Table 3). Several studies on former mines in the French Massif Central and other countries have yielded results of the same order of magnitude, e.g. 400 mg Pb kg⁻¹ (Bodénan et al. 2004), 774 mg kg⁻¹ (Courtin-Nomade et al. 2012), 5,091 mg kg⁻¹ (Ye et al. 2001) and 15,200 mg kg⁻¹ (Wanat et al. 2013). Regarding zinc tailing contents, 1,064 and 786 mg kg⁻¹ were respectively found for T1 and T2. In comparison, these values average between 119 and 12,563 mg kg⁻¹ in the literature (Ye et al. 2001; Bodénan et al. 2004; Courtin-Nomade et al. 2012). In the case of arsenic (As), tailing sample concentrations are less than Pb and Zn (respectively 354 and 325 mg kg⁻¹ for T1 and T2). These As concentrations are relatively low compared to similar study sites: 6,054 mg kg⁻¹ and sometimes even reaching 83,000 mg kg⁻¹ (Bodénan et al. 2004; Wanat et al. 2013). Along the same lines, antimony (Sb) concentrations amount to 196 mg kg⁻¹ for T1 and 157 mg kg⁻¹ for T2. These values remain very low compared to the literature, which reports some values of up to 11,560 mg kg⁻¹ (Courtin-Nomade et al. 2012). Greater concentrations in both Pb (38,412 mg kg⁻¹) and Sb (363 mg kg⁻¹) were observed in the T3 sample, whereas concentrations in Zn (1,309 mg kg⁻¹) and As (330 mg kg⁻¹) are of the same order of magnitude as the tailings. For the filling path (T4), the Pb, Zn, As and Sb contents were respectively 15,686, 1,177, 592 and 228 mg kg⁻¹. These values lie close to those of tailings T1, except for the recording of a major Sb enrichment.

As expected, sediments (Sed) near the riverside show high metal(loid) contents: 12,675, 652, 189 and 195 mg kg⁻¹ for Pb, Zn, As and Sb, respectively. These values are much higher relative to the geochemical background (Grosbois et al. 2012) and median European stream sediments (Salminen 2005). Moreover, over 1 m of riverside, the metal(loid) contents are roughly

4,973, 597 and 135 mg kg⁻¹ for Pb, Zn and Sb, respectively (data not shown). Another study on downstream river sediments conducted by Cottard (2010) indicated concentrations of Pb, Zn and As (Sb was not measured) much lower and nearer the geochemical background: 383, 201 and 110 mg kg⁻¹, respectively.

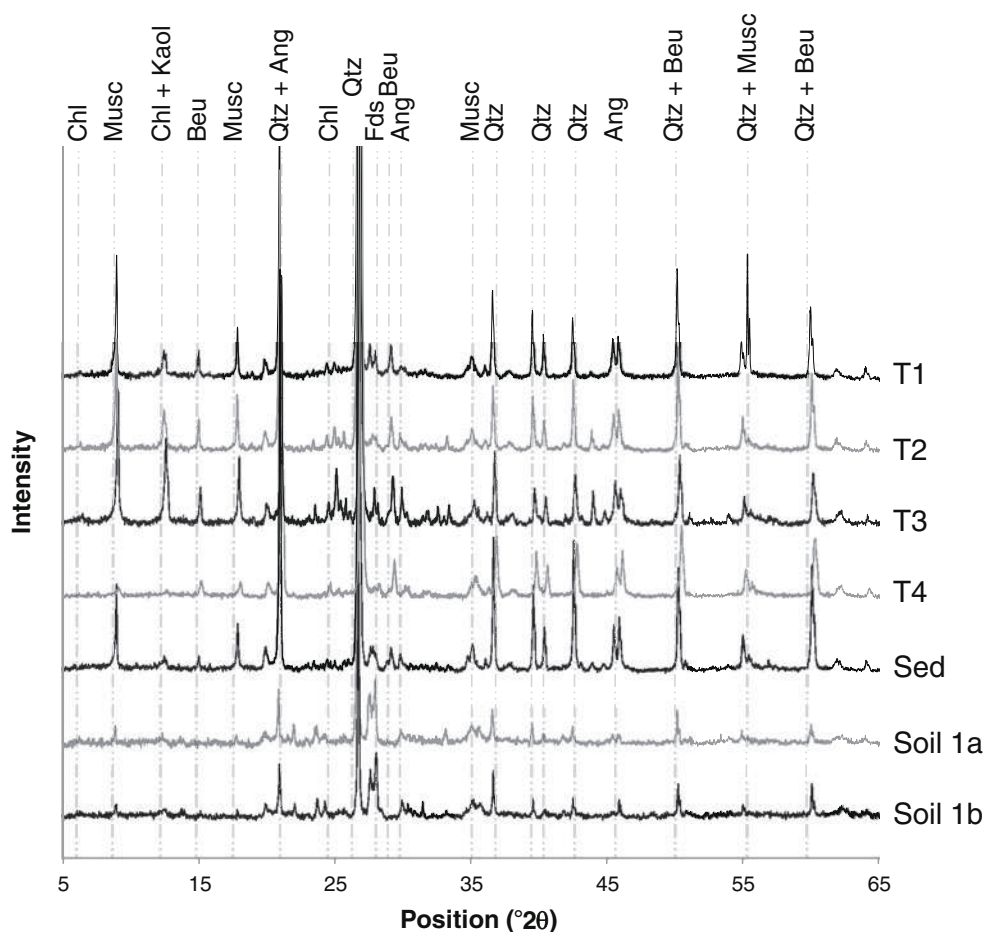
With respect to the soil samples, Pb contents are 2,930 and 2,780 mg kg⁻¹ for soils 1a and 1b. In contrast, Zn seems to be more heavily concentrated than Pb on the soccer field, as the contents are nearly identical to those observed for the mine waste deposit (up to 950 mg kg⁻¹). As and Sb contents however appear to be slightly lower than those of the deposit, with values typically one-third less (250 mg kg⁻¹ for As and 150 mg kg⁻¹ for Sb). Regardless of the particular element, the contents are considerably higher than the natural background (Baize 1997; Reimann et al. 2003; Diomides 2005; Wilson et al. 2010) and playgrounds/recreation parks in several cities of the world (Carr et al. 2008; Elom et al. 2013). Many soccer field contamination sources are making contributions: (1) the side paths have been laid from waste tailings, which has led to spreading pollution towards the soccer field from particles, notably under shoes; (2) surface input from runoff and wind deposits of tailing particles and (3) topsoil has been many times disturbed during the grass maintenance.

Independent of the elements and samples, the metal(loid) contents exceed the predicted values of no-effect concentrations of soils (PNEC_{soil}—12 mg kg⁻¹ for Pb, 24 mg kg⁻¹ for Zn, 1.6 mg kg⁻¹ for As, and 37 mg kg⁻¹ for Sb, Smolders et al. 2009; Reimann et al. 2010), thus corresponding to the values that define the threshold used in environmental risk assessment. These results therefore suggest a significant contamination around the mine waste deposit in each environmental compartment (sediments and soils) surrounded by the hydric and aerial vectors.

Mineralogical characterization

The XRD and SEM-EDS analyses are reported in Figs. 2 and 3, respectively. XRD results clearly show, for all samples, that the

Fig. 2 XRD patterns of the study samples (tailings, sediments and soils). *Musc*: muscovite; *Kaol*: kaolinite; *Chl*: chlorite; *Qtz*: quartz; *Fds*: feldspar; *Beu*: beudantite; *Ang*: anglesite



mineralogical background corresponds to quartz (SiO_2), orthoclase (KAlSi_3O_8) and phyllosilicates, such as muscovite ($\text{KAl}_2(\text{OH})_2\text{AlSi}_3\text{O}_{10}$), chlorite ($(\text{Mg,Fe,Mn,Al})_{12}((\text{Si,Al})_8\text{O}_{20})(\text{OH})_{16}$) and kaolinite ($\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$). The quartz and muscovite constitute the major phases in terms of a semi-quantitative approach (Table 4). As expected, T3 and T4 are enriched in clay (i.e. depending on topography), whereas the amount of quartz decreases. These results are consistent with the grain size fractions (Table 3). The fine clay particles are leached by runoff (e.g. producing a stormwater impact) in accordance with a standard sedimentary logic. As regards the soccer field surface, the mineralogy is dominated by the same solid phases (i.e. quartz, micas, feldspars, kaolinite and chlorite), which is consistent with these soil materials. The presence of barite is also to be noted.

For all samples, the major metal(loid)-bearing phases are anglesite (PbSO_4) and beudantite ($\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$); from a semi-quantitative XRD, these represent overall about 6 and 1 % respectively of all samples (data not shown), with the T3 samples being the leading bearing phases. The SEM-EDS analyses serve to confirm the XRD results, in addition to highlighting the presence of less crystallized bearing phases, like lead oxides (PbO), Fe-oxyhydroxides, Zn/Fe-oxyhydroxides and Pb/Fe-oxyhydroxides (Fig. 3). Zn

however seems to be slightly diffuse. Moreover, Sb-bearing phases could not be identified due to: (1) the small concentration in each sample and (2) the very diffuse characteristic of Sb. Recently, Joussein et al. (2013) showed that Sb is associated with the beudantite structure in an old mine site from the Limousin region (French Massif Central). Lastly, based on the proportion of mineral phases derived from XRD and SEM-EDS, the metal(loid)-bearing phases are distributed relatively homogeneously over the tailing and sediment samples. Concerning the soccer field, the presence of beudantite and anglesite is effective but in smaller amounts and any lead oxides was detected in topsoils. A large number of bearing phases are correlated with the presence of amorphous-bearing phases (mainly metal(loid)-rich Fe-oxyhydroxides and organo-mineral matrix). The geochemical distribution of metal(loid)s in each sample provides an understanding of their behavior and stability over time.

Geochemical compartmentation in solid sample metal(loid)s

Sequential extractions (BCR)

The distribution of Pb, Zn, As and Sb fractions is shown in Fig. 4. The exchangeable fraction (F1) corresponds to the

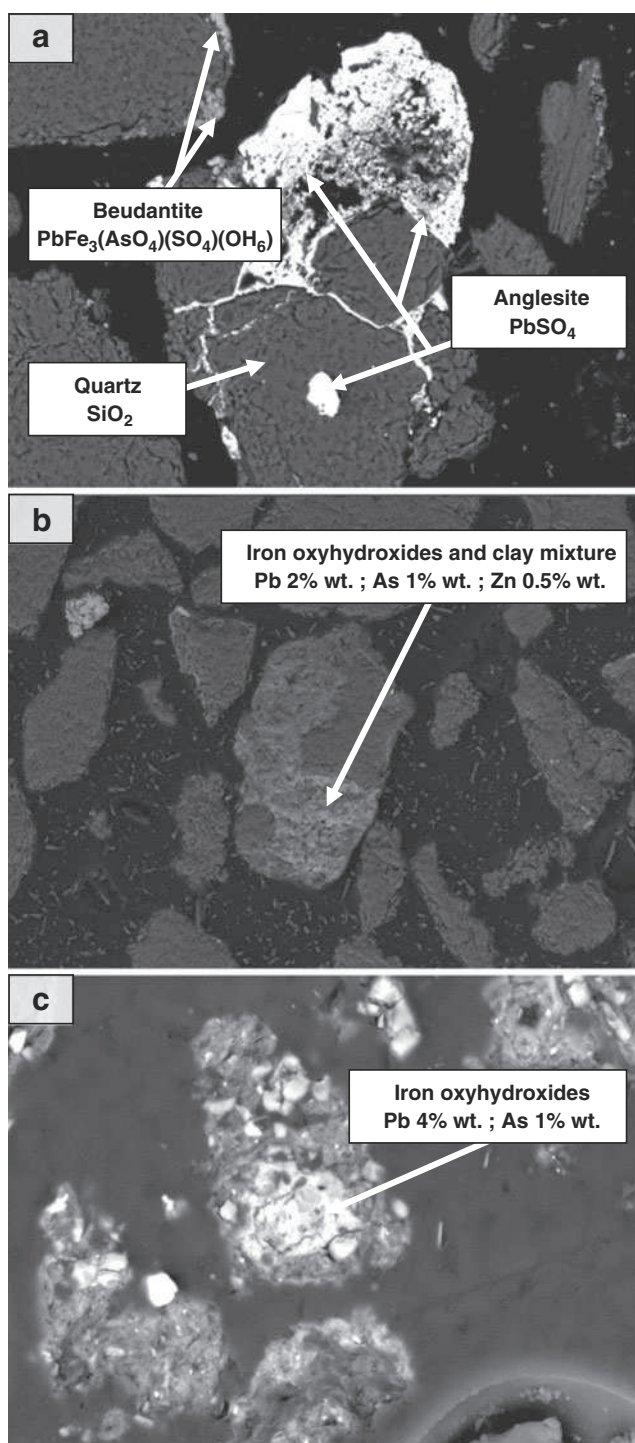


Fig. 3 SEM-EDS photography in BSE mode: **a** tailing, **b** sediment and **c** soil samples

easily soluble metal fraction. These labile Pb contents represent 1 to 13 % of total Pb concentrations; therefore, a non-negligible share is effective for the labile Zn with values ranging from 0.4 to 19 %. These results are in agreement with the literature, which indicates a Pb percentage in F1 typically ranging from 0 to 15 % and from 0 to 40 % for Zn (Cappuyns

Table 4 Evolution in minerals, as estimated by the relative intensities of XRD reflections for all samples studied

	T1	T2	T3	T4	Sed	Soil 1a	Soil 1b
Quartz	a	a	a	a	b	a	a
Orthoclase	c	c	c			d	d
Muscovite	b	b	b	d	b	d	d
Kaolinite	d	d	b	c	d	c	c
Chlorite		c	c			c	c
Beudantite	d	d	d	d	d	c	c
Anglesite	d	d	d	c	c	c	c

^a Predominant

^b Dominant

^c Minor

^d Abundant

et al. 2007; Rodriguez et al. 2009). Conversely, the maximum values obtained for As (0.6 %, Sed sample) and Sb (0.4 %, T3 sample) in exchangeable form are very low, as previously observed in other studies (Fotovats and Naidu 1998; Pérez-Cid et al. 1998; He 2007).

The fraction corresponding to the rather poorly crystalline Fe/Mn oxyhydroxides and sulfates is called the reducible fraction (F2). For Pb, the share of this fraction accounts for 3 to 25 % of total content. These values seem to be similar to those previously found in the literature (between 20 and 40 %, (Cappuyns et al. 2007; Álvarez-Valero et al. 2009). This result is also in agreement with the mineralogical characterization (see above). Anglesite, which is a Pb-sulfate, and Pb/Fe-oxyhydroxide mixtures have been derived from the SEM analyses (Fig. 3). Similarly, the Zn percentage in F2, which amounts to between 0.5 and 11 %, lies within the range presented in the literature (Álvarez-Valero et al. 2009; Rodriguez et al. 2009). The relation between Zn and Fe-oxyhydroxides, as highlighted in the SEM analyses, explains the significance of these values especially for the topsoils. The amounts of As and Sb for the F2 fraction are relatively low to near-zero (recorded at 0.2 and 0.02 % for As and Sb, respectively). These values are low comparatively to the literature, which reports around 5 to 10 % for As and 0 to 5 % for Sb (He 2007; Álvarez-Valero et al. 2009).

Third fraction extractions (F3) show that Pb is associated, for 20 % on average, with the oxidizable fraction (Fig. 4), which corresponds to the organic matter and sulfides. Since no Pb-sulfides, like galena (PbS), have been identified during the solid characterization, only the role of organic matter is to be taken into consideration. This role is clearly apparent for the soccer field samples, which are rich in organic matter (up to 30 % Pb for the F3 fraction). Zinc contents seem to be lower than the observed literature data (i.e. around 10 % Rodriguez et al. 2009); 0.5 to 1 % of Zn is associated with the F3 fraction

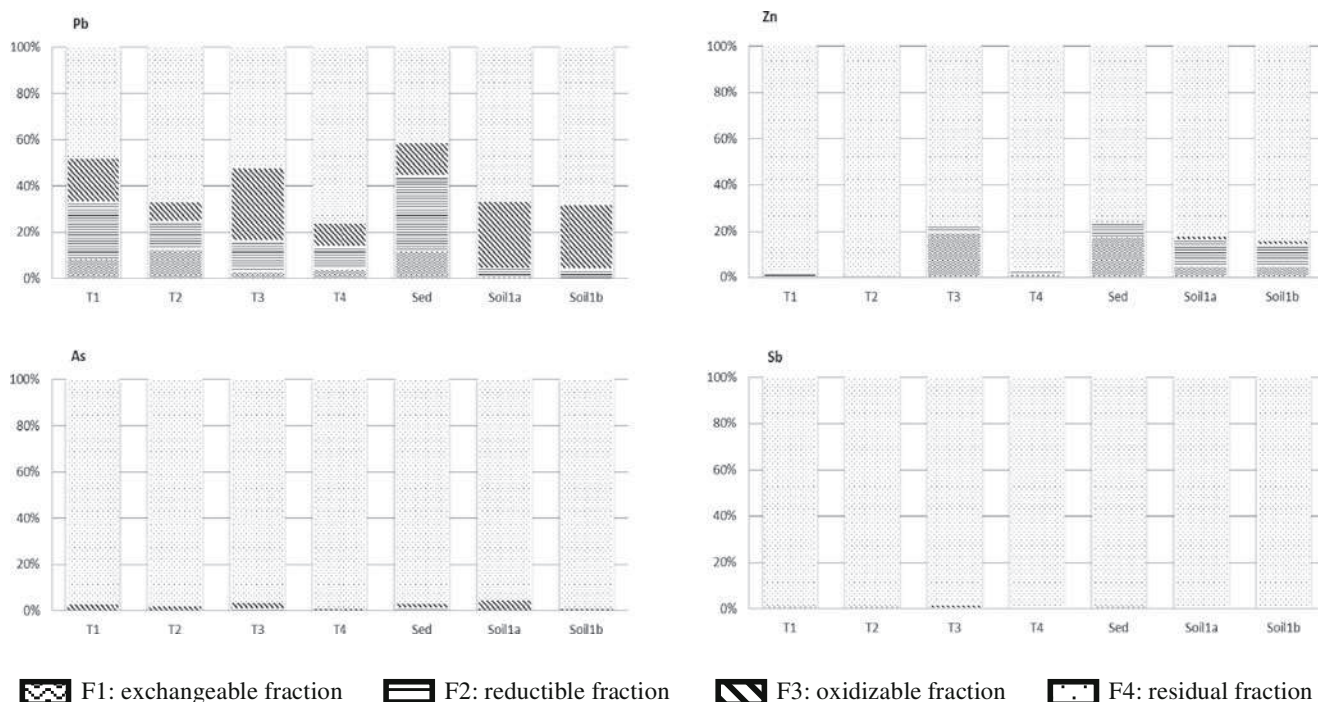


Fig. 4 Distribution of Pb, Zn, As and Sb according to the selected sequential extraction protocol (BCR)

(Fig. 4). In all likelihood, the diffuse presence of Zn can be correlated with the presence of organic matter and iron oxyhydroxides. Arsenic exhibits a very slight tendency to be found with the oxidizable fraction since the values encountered range from 1 to 4 %, which is low compared to the literature (Álvarez-Valero et al. 2009). The Sb part in F3 remains negligible (0.5 to 1 % at most), as already demonstrated in literature for other mining sites (Anju and Banerjee 2010).

The residual fraction is the most stable, i.e. with metal(loid)s linked to the crystal structure and non-attackable by the F1, F2 and F3 fractions. The values obtained equal roughly 40 to 70 % for Pb, 75 to 98 % for Zn and 95 % to nearly 100 % for As and Sb (Fig. 4). These results indicate that As and Sb are mainly concentrated in the residual fraction, considered to be long-term stable with a very low risk of contaminant release into the environment. In this study, the major As- (and Sb-) bearing phase is beudantite, which is very stable according to the works of Frentiu et al. (2009), Frost et al. (2011) and, more recently, Joussein et al. (2013) in mining-related contexts.

BCR extractions are currently used to evaluate the potential environmental risk relative to metal(loid) compartmentation: it is commonly accepted that the metals associated with the residual fraction are potentially weakly mobilized and bio-available. In this instance, the compartmentation of elements differs: Pb and Zn are significantly spread across all BCR fractions, whereas As and Sb are primarily associated with the residual fraction. Moreover, since no modification of the As and Sb chemical speciation has been highlighted among all samples (tailings, soccer field soils and sediments), it can be

concluded that the presence of the As- and Sb-bearing phases in soils and sediments is due to hydric transfer relative to runoff events or, albeit to a lesser extent given the context, to wind deposits. Moreover, the nature of As/Sb-bearing phases does not change during transfer. Therefore, the metals remain associated with these same phases during transport from tailings to topsoil or sediments. This fact induces non mobile characters of these two elements in topsoil.

Metal(loid) human bioaccessibility

Bioaccessibility results are listed in Table 5. These results expose the modification in terms of bioaccessibility: (1) between tailings or sediments and soils samples and (2) between gastric and intestinal bioaccessibility. The same behavior however can be found between As–Sb and Pb–Zn, which matches the findings of BCR experiments.

Pb bioaccessibility from gastric phase extraction depends on the sample origin and ranged from 7.2 to 40.6 % (Table 5). In tailings T1 and T2, Pb bioaccessibility was around 20 %. For the sediment samples, Pb gastric bioaccessibility ranged between 7.2 and 19.0 %. The highest Pb gastric bioaccessibility is effective for soccer field soil samples, with approx. 40.6 % (soil 1a) and 39.8 % (soil 1b). These values are relatively low compared to those obtained in a mining context (Smith et al. 2011) and can be explained by the relative stability of beudantite. Regarding the intestinal phase, the values are spread from 3.3 to 10.7 %, which agrees closely with the literature (Smith et al. 2011). The Pb gastric

Table 5 Determination of Pb, Zn, As and Sb bioaccessibility

Sample	Pb bioaccessibility (%)		Zn bioaccessibility (%)		As bioaccessibility (%)		Sb bioaccessibility (%)	
	Gastric phase	Intestinal phase	Gastric phase	Intestinal phase	Gastric phase	Intestinal phase	Gastric phase	Intestinal phase
T1	21.5±1.3	5.3±0.8	1.9±1.3	0.9±0.1	11.3±1.3	11.2±0.3	<DL	<DL
T2	23.3±0.7	3.4±1.3	1.7±0.7	0.9±0.1	4.9±0.7	7.1±0.3	<DL	<DL
T3	7.2±0.4	3.3±0.3	23.1±0.4	13.6±0.2	6.4±0.4	8.7±0.4	<DL	<DL
T4	13.6±0.9	5.9±0.9	2.6±0.9	1.8±0.2	2.3±0.9	3.1±0.1	<DL	<DL
Sed	19.0±0.5	10.7±1.6	30.7±0.4	25.5±3.2	5.3±0.4	10.8±5.4	<DL	<DL
Soil 1a	40.6±0.4	7.3±0.5	28.5±0.4	5.1±0.2	7.6±0.4	8.4±0.1	<DL	<DL
Soil 1b	39.8±1.8	6.7±0.2	26.9±1.8	4.9±0.3	6.0±1.8	8.1±0.5	<DL	<DL

DL detection limit

bioaccessibility observed for soils is generally on the order of 60 %, whereas intestinal bioaccessibility ranged from 2 to 10 % (Juhasz et al. 2011; Smith et al. 2011). It is well-known that the toxic effect of a metallic or semi-metallic element depends on its chemical speciation. According to BCR extractions, Pb was distributed in the four fractions, with an upper trend line for the more stable fraction (residual fraction, see Fig. 4). These results are therefore consistent. The real risk to human health is determined by comparing Pb bioaccessibility, soil content and the Pb tolerable daily intake (TDI). This TDI measure corresponds to the smallest human intake without any risk chronic effects occurring; it is usually expressed on the basis of body weight in microgramme per kilogramme of body weight per day. Since TDI_{Pb} equals $0.15 \mu\text{g kg bw}^{-1} \text{day}^{-1}$ (Winter-Sorkina et al. 2003), this value represents $7.5 \mu\text{g/day}$ for a human weighing 50 kg. The accidental ingestion of 1 g of soccer field soil can, according to the worst case scenario, deliver in an adult body 50 % of 2,930 $\mu\text{g Pb}$ (Table 3), thus 1,451.5 μg , which greatly exceeds the reference TDI_{Pb} . This value would increase in the case of a child's ingestion. Consequently, the Pb health risk is significant even if an accidental 1 g daily ingestion of soil proves to be relatively improbable.

The Zn gastric bioaccessibility and intestinal phase ranged from 1.7 to 30.7 % and 5.1 % and 4.9 %, respectively, with the highest percentage obtained for the soccer field. These values are relatively low compared to literature data (Turner et al. 2009). In addition, a comparison of the Zn bioaccessible part for all samples corroborates the values obtained in BCR extraction (Table 5 and Fig. 4). Total bioaccessibility corresponds on average to 35 %. Since Zn is a micronutrient, TDI_{Zn} is greater than TDI_{Pb} : $TDI_{Zn}=0.6 \text{ mg kg bw}^{-1} \text{day}^{-1}$ (Okorie et al. 2012). The soil content amounts to $2,930 \text{ mg kg}^{-1}$, thus for an ingestion of 1 g, only 1,025.5 μg are accessible, which represents 3 % for a 50-kg human TDI. In this context, therefore, Zn does not constitute a health risk in the soccer field nor in the site context (tailing, soil and sediment samples).

The As gastric bioaccessibility varied from 2.3 to 11.3 %, and the range was similar for the intestinal phase. As opposed to Pb bioaccessibility, higher values were observed for the T1 sample (up to 11 % for both phases, compared to 6.0–8.4 % in the soccer field soil samples). The 14.3 % average of total As bioaccessibility means that As-bearing phases are fairly stable, which is in agreement with the mineralogical and BCR results (beudantite phase; see above). As regards the health risks associated with the presence of As, TDI_{As} is equal to $0.3 \text{ mg kg bw}^{-1} \text{day}^{-1}$ (Okorie et al. 2012), which corresponds to $0.015 \text{ mg day}^{-1}$ for a 50-kg human. One gram of soccer field soil samples can thus deliver 14.3 % of 0.261 mg of As (Table 3), i.e. 0.037 mg of As. This amount is 2.5 times greater than the TDI value; consequently, even if As bioaccessibility remains very low, the acute toxicity risk is in effect for As due to its high toxicity level.

In this study, Sb bioaccessibility appears to be nonexistent. This result is not in accordance with the limited literature available for this element. In the mining context for example, Denys et al. (2009) observed a Sb bioaccessibility ranging from 1 to 10.8 %. The difference with this study pertains to the difference in Sb-bearing phases. In this study, Sb is in fact associated with the beudantite structure, which as confirmed by results is stable (see BCR experiments above and Joussein et al. 2013). No human health risk can thus be attributed to the Sb element.

Generally speaking, the metal(loid) bioaccessibility approach herein matches the results obtained in previous surveys. The direct health risk is certain for Pb and As elements, in particular on the type of soccer field classically used for sports and recreation.

Conclusion

This study has highlighted the environmental and health impacts of mining wastes enriched with Pb, Zn, As and Sb. The metal(loid)-bearing particles are slowly dispersed from tailing

waste materials into the surrounding environment (sediments and soils) mainly by runoff (hydraulic) transport and, to a lesser extent, by wind deposits. Moreover, the health risk assessment is indeed pertinent and increasing over time, since the site's periphery is currently being used: (1) as an active soccer field and (2) for swimming in the river during the summer season. In accordance with the mineralogical characterization of the various metal(loid)-bearing phases, BCR extraction results demonstrate that As and Sb are mainly associated with stable minerals in the residual fraction, whereas Pb and Zn are quite evenly distributed across the various soil fractions. The potential health risk induced by solid particle ingestion, assessed using measured metal(loid) bioaccessibility values, is in perfect agreement with the speciation analysis. More specifically, Pb and Zn are relatively bioaccessible as compared to As and Sb. The health risks associated with accidental soccer field or material ingestion should thus be taken into account since the 64,000 m³ of tailings represent even today a major contaminant dispersion risk. Moreover, due to the sizable tailing ponds, it can be reasonably assumed that airborne particle inhalation could increase the exposure to metal(loid)s since motocross and biking activities are also currently being practiced on the site.

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