



# Trace metal(loid) mobility in waste deposits and soils around Chadak mining area, Uzbekistan

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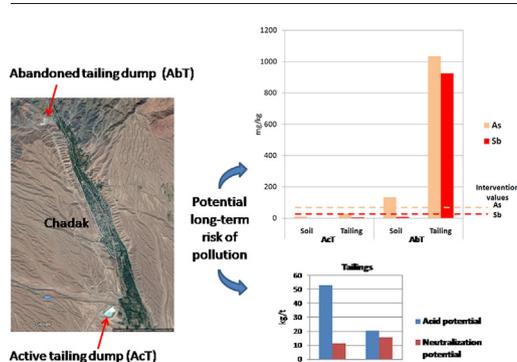
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## HIGHLIGHTS

- Total concentrations of As and Sb strongly exceed the intervention values in abandoned wastes.
- Selective extractions showed As and Sb with relatively high potential mobility.
- Zn and Pb mobility was controlled by cation exchange capacity of clay particles.
- Precipitation of Ca–Fe(III)–AsO<sub>4</sub> phases was first observed in Chadak mine wastes.
- Long-term pollution will be mainly controlled by tailing oxidations processes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The assessment of potential trace metal(loid) contamination in tailing dumps and soils was characterized in the Chadak mining area (Uzbekistan). Concentrations of trace elements (V, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb) were determined by X-ray fluorescence analysis and compared with background and intervention values (IV). The concentrations of As, Zn, Sb, and Pb were higher in the abandoned than in the active tailing dump, ranging from 42–1689 mg/kg for As, 73–332 mg/kg for Zn, 14–1507 mg/kg for Sb, and 27–386 mg/kg for Pb. Selective extractions were applied in order to assess the mobility and availability of trace metal(loid)s in samples. Oxyanion-forming elements such as As and Sb were immobilized by Fe oxides, although to some extent also extractable with acetic acid and soluble-in-water forms were detected, indicating potential bioavailability that can impose a potential toxicity risk for the environment. Selective extractions data also showed that Zn and Pb were relatively immobile, although in higher contamination sites significant amounts of these elements were also extractable with acetic acid. In tailing materials Zn and Pb mobility were negatively correlated by the cation-exchange capacity (CEC) and clay content, indicating the importance of these factors in the reduction of the potential toxicity for these elements. Total concentration of As, Sb, and Pb were also negatively correlated with soil pH, indicating that the oxidation process of sulphide tailings and thus the generation of acidic conditions may lead to release of contaminants over time. However, due to the calcium carbonate content, the acid neutralization capacity of the tailings is not yet exhausted and contaminant concentrations in soil-pore water are still relatively low. The results of our investigation suggest that environmental risk associated with these wastes in semi-arid climate is therefore not a short-term problem but rather requires constant monitoring and additional ecotoxicological studies.

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## 1. Introduction

The increase in mining activities in recent decades inevitably exerts a negative influence on the environment. The exploitation of mineral resources results in the production of large volumes of mining wastes containing metals or metalloids at elevated concentrations (Lottermoser, 2010). In particular, open-pit mining activities may therefore have a negative environmental impact on soils and watersheds. Sulphide-rich minerals represent a major ore deposit for extracting metal(loid)s worldwide, generating millions of tonnes of tailings and acid mine drainage (Dudka and Adriano, 1997). The major concern of contamination of soil, sediments, and waters by trace metals is their toxicity and threat to human life and the environment (Nriagu et al., 2007).

Acid mine drainage (AMD) is one of the most serious environmental problems in sulphide mineralized areas, causing the solubilization and dispersion through the environment of trace metals and related toxic elements (Astrom, 1998). Most of the environmental-impact assessment and remediation efforts related to AMD generation have been focused on temperate climates, and few on mine sites exposed to semi-arid climates where AMD is not an immediate problem (Razo et al., 2004; Hayes et al., 2012). In these areas, the presence of soils with high buffering capacity is common, and when the AMD infiltrates the soil, the acidity is neutralized and most of the pollutants precipitate (Simón et al., 2005). In any case, although AMD generation in a semi-arid climate is not a short-term problem, the pollution can persist for thousands of years due to the slow time course of the processes related to oxidation, hydrolysis and acidification (Kempton and Atkins, 2000), which poses a long-term risk and even a chemical time-bomb for environment and human health.

Metal(loid)s are transferred to the environment via fly ash, dust, and leachates coming from point-source pollution such as mine quarries, dumps, and tailings (Shukurov et al., 2014; Martín et al., 2007), and may become a problem of diffuse pollution due to the widespread partitioning of these elements through the ecosystem (Martín et al., 2010). It is now widely recognized that the mobility and bioavailability of trace metals in soils depend not only on the total concentration, but also on their specific chemical form or binding state in relation to soil properties and constituents (Dang et al., 2002; Sauve et al., 2000; Nyamangara, 1998; Romero-Freire et al., 2014). However, changes in environmental conditions such as acidification, changes in the redox-potential conditions or increases in organic-ligand concentrations can result in trace-element mobilization from the solid to the liquid phase and cause contamination of surrounding waters (Gleyzes et al., 2002).

To assess the mobility and bioavailability of potentially polluting elements, several extraction schemes have been developed and described in the literature (Rauret et al., 1989; Kersten, 2001; Gleyzes et al., 2002; Quevauviller, 2002). These extraction schemes are based on operationally defined fractions that allow the assessment of distinct reagent-extractable forms (distilled water, single salts, acetic acid, complexing agents, etc.), which are usually defined as pool-extractable forms (soluble, exchangeable, carbonate associated, Fe/Mn oxide-associated, organics associated, residual, etc.). The most insoluble forms (extracted only by strong acids) are usually defined as residual forms (Beckett, 1989). In this way, a set of selective extraction techniques are used to determine the most leachable and thus potentially the most bioavailable compounds, while the total abundance of potentially harmful elements was determined by strong acid digestion (Anju and Banerjee, 2010). Despite the uncertainties associated with non-selectivity of the extractants, readsorption, and redistribution problems, extraction schemes remain widely used as an essential tool in element fractionation in soil and sediments (Kersten, 2001; Gleyzes et al., 2002).

The present study is focused on the Chadak mining area, one of the main gold-producing sites in Uzbekistan. The Chadak ore area has been known since antiquity and was in use up to the 12th century, with mining traces (abandoned open-pit mines and placer fields) preserved in the lower Chadak village and other surrounding

areas. However, in the 12th and 13th centuries the mining activity declined and was revived only in the 20th century (Kuldashev and Abdurahmanov, 2009). In this study, the total concentration and distribution of metal(loid)s are determined in soils and waste deposits in and around the tailing dumps of Chadak mining area, and the mobility and potential bioavailability of the main contaminants by selective chemical extractions are assessed, with the aim of evaluating the potential risk of pollution as the first step in an environmental risk assessment of the area.

## 2. Materials and methods

### 2.1. Study area

Samples were collected from the vicinity of the Chadak ore field located in the Pap district of Namangan region at the southern slopes of the Kurama ridge in Chadak basin (eastern Uzbekistan, Fig. 1). Chadak ore field includes gold silver deposits (Pirmirab and Guzaksay) and a number of other exploitable minerals. The gold silver veins of the Chadak deposits are of low sulphidation type hosted by Carboniferous andesite volcanites and are associated with quartz-sericite-pyrite type alteration. The main gangue minerals are quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>), adularia (KAlSi<sub>3</sub>O<sub>8</sub>), sericite (KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>2</sub>), wollastonite (CaSiO<sub>3</sub>), and tremolite (Ca<sub>2</sub>(Mg,Fe)<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>). The main ore minerals are pyrite (FeS<sub>2</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>), but galena (PbS), chalcocopyrite (CuFeS<sub>2</sub>), and sphalerite (ZnS) are also common (Smirnova et al., 2009).

The area is characterized by a relatively well-developed mining industry, operated since 1970 by the Chadak gold-extracting plant (GEP) with the capacity of 180,000 t/y. The plant treats gold-bearing ore from the Pirmirab and Guzaksai deposits. Mining is conducted by both an underground and open-pit method, and two tailing dumps were established to store the waste from the mineral-extraction procedures. The first tailing dump, which operated from 1970 to 1979, is now abandoned (AbT), while a new tailing dump has been operating since 1979 and is still active (AcT). According to Filimonov (2009), the wastes stored in tailing dumps amount to as much as 3 Mt. The technological ore-extracting scheme includes: three-stage crushing, one-stage milling in a closed cycle with a two-stage ore classification and hydrocyclone overflow thickening; cyanidation of thickened product; filtration of gold-bearing solutions; precipitation of precious metals (Au and Ag) onto zinc dust; and drying of the zinc precipitates. The tailing waste products, after sterilization with liquid chlorine, are delivered to a dump for storage (Smirnova and Shamaev, 2012).

Production facilities of the mining group includes: mines, beneficiation plant, tailing dumps, and administrative-domestic premises. Two villages, Oltinkon and Chadak, are located on the banks of the Chadak-Sai river (Fig. 2A). Oltinkon is located close to the Chadak GEP and upstream from the abandoned tailing dump, while Chadak is located between the two tailing dumps. The river Chadak-Sai is the only source of water for mining processes, but also for residents of the villages on its banks.

### 2.2. Soil sampling and sample preparation

Samples were taken in a systematic pattern (100 × 100 m grid) from the upper soil layer (0–10 cm) around the two tailing dumps, and from the surface layer of both the abandoned (AbT, Fig. 2B) and active (AcT, Fig. 2C) tailing dumps. A vertical profile of 1.5 m deep was also sampled in the abandoned tailing dump (A: 0–30, B: 30–80, C: 80–150 cm). A total of 40 samples were collected from both areas. Samples were placed in polyethylene bags and transported to the laboratory for physico-chemical analyses. Samples were air-dried at room temperature, sieved through 2-mm mesh, ground, and homogenized in an agate mortar. Powder pellets for X-ray fluorescence analysis were prepared under a



Fig. 1. Location map of the study area.

pressure of 7 t with an epoxy-resin admixture in 30-mm dies by a hydraulic press (Herzog, Germany).

### 2.3. Chemical and mineralogical analysis

The main physico-chemical properties of the samples were measured by standard soil-analysis techniques (MAPA, 1994): the pH was measured by a pH-meter (CRISON digit 501) in a 1:2.5 (w/v) soil-water suspension; electrical conductivity (EC) was measured using a EUTECH XS Con 700 m in extracts prepared by filtering 1:10 soil-water suspensions through 0.45- $\mu\text{m}$  cellulose acetate membrane filter; organic carbon (OC) was determined by wet oxidation method; cation-exchange capacity (CEC) was determined by 1 N sodium acetate solution at pH 8.2 measured by atomic absorption spectroscopy using a VARIAN SpectrAA 220FS instrument; particle-size distribution was determined by the pipette method; and calcium carbonate content was determined manometrically upon HCl digestion. The neutralization potential (NP) of tailing samples were evaluated with the modified Sobek acid-base accounting (ABA) method (Lawrence and Scheske, 1997). The acid potential (AP) and net neutralization potential (NNP) was calculated according to SRK (1989).

The total concentration of trace elements (V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, Sb) was measured using X-ray fluorescence (XRF) analysis of the powder pellets (MagiX Pro XRF with rhodium anode X-ray tube). The total concentration of major elements was determined by XRF using glass pellets of subsamples melted with lithium tetraborate fluxer

(0.6:5.5). QA/QC criteria were fulfilled by the use of geochemical standard reference materials GSS-2 and GSS-4 (Table S1, Supporting Information); the experimental average values ranged within the certified reference values in both cases.

Selective extractions were applied to assess trace metal(loid) mobility in sieved samples (<2 mm) at the abandoned tailing dumpsite (AbT) with the following reagents: 1) distilled water (Sposito et al., 1982), 2) ammonium nitrate 1 M (DIN 19730, 1995), 3) acetic acid 0.43 M (Ure et al., 1993), and 4) oxalate buffer pH 3 (Schwertmann and Taylor, 1977). The total concentration of trace metal(loid)s was determined additionally by strong acid digestion ( $\text{HNO}_3/\text{HF}/\text{HCl}$ ). All extracted fractions were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) in a Perkin-Elmer Sciex-Elan 5000 instrument equipped with quartz torch, nickel sampler, and skimmer cones. Standard solutions were prepared from ICP single-element standard (Merck, Darmstadt, Germany) after appropriate dilution with 10%  $\text{HNO}_3$ . The accuracy of the method was evaluated by six replicate analyses of the certified reference material SRM 2711, average recoveries of the certified reference values ranged between 91% and 105% for the main pollutant elements (Martín Peinado et al., 2015).

Selected subsamples were prepared for scanning electron microscopy (SEM SUPRA40VP, ZEISS, Germany). The imaging was performed at an acceleration voltage of 30 kV in both conventional secondary electron and backscattered electron mode. For the elemental microanalysis of mineral particles, an energy-dispersive X-ray (EDX) spectrometer (model AZTEC 2.4, Oxford instruments, UK) was used in pinpoint

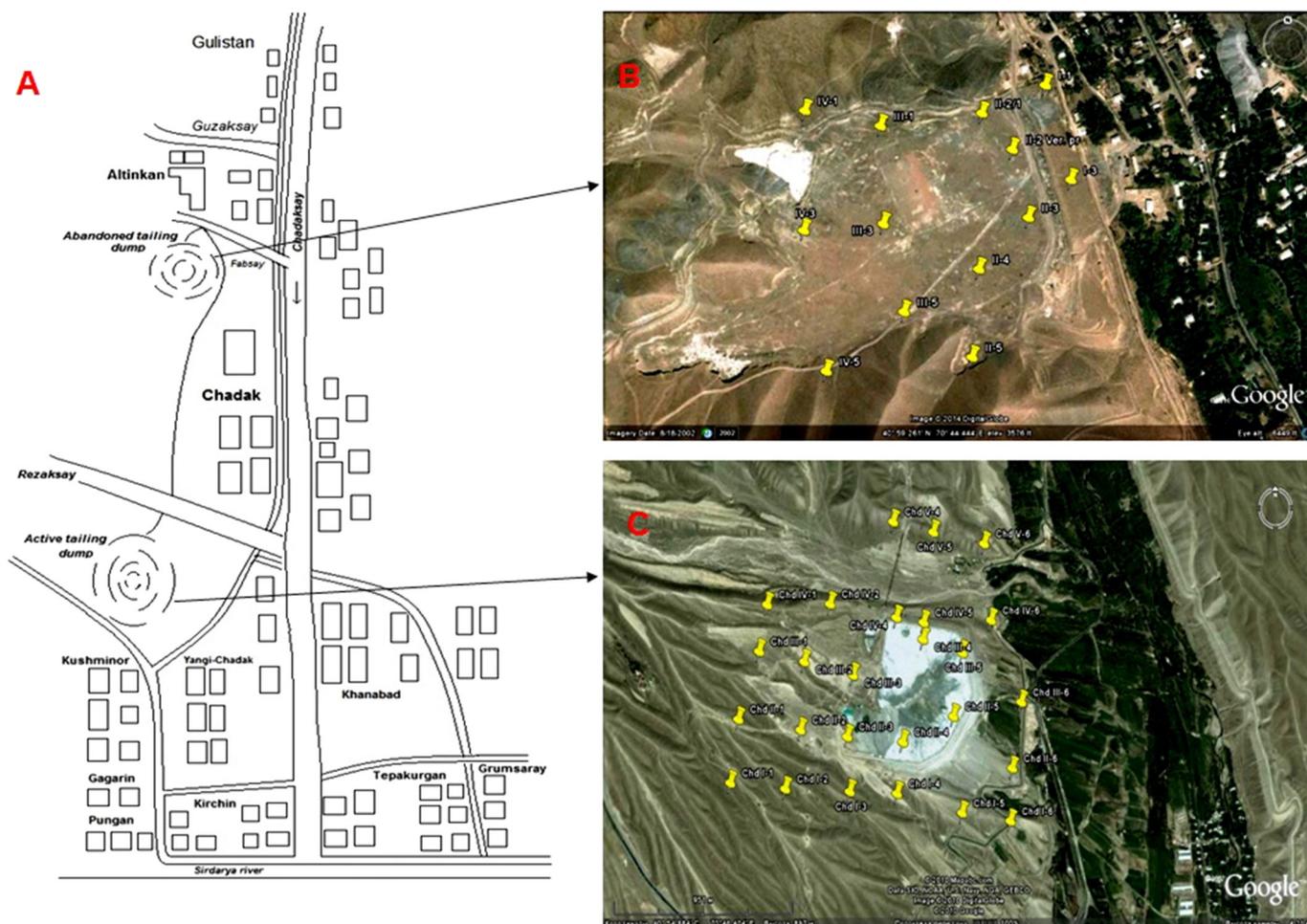


Fig. 2. Location of the samples collected. A: General view; B: abandoned tailing dump (AbT); C: active tailing dump (AcT).

mode (diameter  $1 \mu\text{m}$ ), resolution of  $10 \text{ eV/channel}$ , and a full-spectrum collection time of  $100 \text{ s}$ .

#### 2.4. Statistical analyses

Geochemical background values of trace metal(loid)s for the study area were calculated from surrounding soil samples collected near the tailing dumps using mean ( $M_f$ )  $\pm$  twice the standard deviation ( $\sigma$ ) of the calculated distribution functions (Matschullat et al., 2000).

Statistical analyses of the data were carried out after evaluating the data set for normal distribution by a Kolmogorov-Smirnov test. Mean comparison study was made by one-way analysis of variance (ANOVA) and Tukey's test, where significant differences were considered when  $p < 0.05$ . The relationship between normally distributed variables was investigated using Varimax-rotation principal-component analysis (PCA). All statistical treatments were made using SPSS v.20.0 software.

### 3. Results and discussion

#### 3.1. Soil properties

The general physico-chemical properties of soils and tailing samples are summarized in Table 1, and the properties of the vertical profile collected on AbT in Table 2. The pH values of soil samples collected in the vicinity of AcT and soils covering AbT showed mean values of 8.2 and 8.4, respectively. The moderately alkaline conditions are presumably related to the presence of carbonate minerals calcite, ankerite, and

dolomite (Iavazzo et al., 2012), and can be also related to the arid climate in the study area. In any case, calcium carbonate content in soil and tailings was moderately low (mean values  $< 15\%$ ), with minimum concentrations in tailings ranging from 2.9 to 4.2%. The presence of S was also detected in tailing samples, with values ranging from 1.70 to 0.45%. Therefore, the tailings possess a neutralization potential (NP) which can be balanced with the acid potential (AP) assessed for a worst case from the total S content (neglecting the minor sulphate mineral content as a product of previous oxidation). The acid-base accounting (ABA) of tailings and concentrates are shown, respectively, in Tables 1 and 2. The acid potential (AP) of tailings for AbT is equal to  $20.3 \pm 4.6 \text{ kg CaCO}_3/\text{t}$ , while for AcT it is  $53.1 \pm 7.8 \text{ kg CaCO}_3/\text{t}$ ; meanwhile the mean neutralization potential (NP) of the tailings amount to  $15.5 \pm 2.9$  and  $11.1 \pm 2.7 \text{ kg CaCO}_3/\text{t}$ , respectively. Thus, the net neutralization potential ( $\text{NNP} = \text{NP} - \text{AP}$ ) indicates that the active tailing dump is potentially acid generating ( $\text{NNP} = -42.0 \pm 6.5 \text{ kg/t}$ ), while the abandoned tailing dump is not ( $\text{NNP} = -4.8 \pm 1.2 \text{ kg/t}$ ), according to the criteria defined by SRK (1989:  $\text{NNP} < -20 \text{ kg CaCO}_3/\text{t}$ ). In this sense, the acidification by sulphide oxidation in carbonate soils was previously reported in other semi-arid areas (García et al., 2009; Sánchez-Marañón et al., 2015), where soils with similar range in  $\text{CaCO}_3$  (3.2–7.6%) and S (0.2–0.8%) showed a sharp decrease in pH from 7.4 to 3.1 after 10 years of continuous oxidation under natural conditions.

Soil samples from both areas showed very low EC values (SSDS, 1993), very low CEC (Marañes et al., 1998), sparse OC content, and a sandy-loam texture, with no significant differences between active and abandoned tailing dumps. Tailings at AcT, registered similar values to soil samples for pH, EC, and OC, but significant lower values for CEC

**Table 1**

Mean and standard deviations ( $n = 3$ ) of general physicochemical properties of surface samples (0–10 cm) in the active (AcT) and abandoned (AbT) tailing dumps. Letters (a, b) indicate significant differences between samples ( $p < 0.05$ ). EC: electrical conductivity; CEC: cation-exchange capacity; OC: organic carbon; AP: acid potential; NP: neutralization potential; NNP: net neutralization potential.

Area	Subarea	pH	EC (dS/m)	CEC (cmol/kg)	CaCO <sub>3</sub> (%)	OC (%)	Clay (%)	Silt (%)	Sand (%)	AP kg/t	NP	NNP
AcT	Soil	8.2 ± 0.2 (a)	0.17 ± 0.04 (a)	10.4 ± 2.7 (a)	4.8 ± 2.6 (a)	1.07 ± 0.90 (a)	12.0 ± 1.6 (ab)	33.4 ± 0.3 (a)	53.1 ± 0.8 (a)			
	Tailing	8.3 ± 0.1 (a)	0.53 ± 0.05 (a)	2.6 ± 1.0 (b)	5.4 ± 1.7 (a)	0.83 ± 0.24 (a)	5.8 ± 0.6 (b)	22.9 ± 5.8 (a)	71.3 ± 6.4 (a)	53.1 (±7.8)	11.1 (±2.7)	−42.0 (±6.5)
AbT	Soil (cover)	8.4 ± 0.2 (a)	0.30 ± 0.44 (a)	7.9 ± 2.3 (ab)	10 ± 1.4 (ab)	0.66 ± 0.30 (a)	13.8 ± 2.9 (a)	35.9 ± 30.2 (a)	50.3 ± 28.6 (a)			

and clay content (Table 1), indicating a selection in the particle size towards the sand fraction and concomitant reduction in clay content that is directly related to the reduction in the CEC (Jung, 2008).

The comparison between tailings from vertical profile in AbT and active tailing dump (AcT) showed similar properties, with no significant differences in any of the main variables studied except CaCO<sub>3</sub>, which showed significantly lower values from the A to C layers (Table 2).

### 3.2. Total trace metal(loid) concentrations

The mean total concentration of trace metal(loid)s in soils and tailings determined by XRF is shown in Table 3. The results were compared with the calculated background concentration (BC) of the soils in the area, and the intervention values (IV) reported by the Ministry of Environment of the Regional Government in Andalusia (Spain), based on a review of the intervention values in many countries worldwide (Aguilar et al., 1999) and the Dutch Target and Intervention Values (RIVM, 2000).

The mean concentrations of V, Cr, Co, Ni, Cu, and Cd in all surface samples (soils and tailings) were in the range of the background concentrations (BC) in the area. On the other hand, Zn, As, Sb, and Pb showed significantly higher mean concentrations (Table 3) both in tailings of AcT (exceeding 1.7-, 1.8-, 0.8-, and 2.8-fold the BC values, respectively), and in the covering soils of AbT (exceeding 1.5-, 8.8-, 1.8-, and 2.6-fold the BC values, respectively).

In the vertical profile of AbT, trace metals V, Cr, Co, and Ni presented significant differences although these values were in the range of BC (Table 3). Layer A had the highest concentrations of these elements, which decreased in the next two layers. On the other hand, concentrations of Cu, Zn, and Cd were slightly above the BC but below the intervention values (IV) and presented no significant differences along the vertical profile. The Pb concentrations in the vertical profile were higher than the BC (between 3.9- and 6.1-fold), but also below the IV. However, the mean values of Zn and Pb revealed an inverse trend in vertical distribution, showing the highest mean concentrations in the deepest C layer. High values of these elements in tailings could be attributed not only to the presence of sulphide and sulphosalt minerals (pyrite, sphalerite, arsenopyrite, galena, and tetrahedrite) in ores of the Chadak deposits but also to the concentration related to the metal-extraction procedure in the mining activity of the Chadak ore field. The two elements with the highest concentrations in all three layers were As and Sb, with mean values strongly exceeding the IV (up to 20-fold for As, and 62-fold for Sb), with the highest concentrations in the surface A

layer (1030 and 920 mg/kg, respectively). A comparison of these concentrations with the ecotoxicological threshold levels reported of 55 mg/kg for As (Van den Berg et al., 1993) and 60 mg/kg for Sb (Sheppard et al., 2005) indicate a high risk of pollution in the area. The problem is exacerbated by the fact that these wastes are located upstream of the main population area (Chadak city), which poses a serious potential pollution risk over time.

### 3.3. Chemical metal(loid) fractionation

Due to the elevated concentrations of As and Sb, and the relatively high concentrations of Zn and Pb in the samples analysed from the vertical profile in the abandoned tailing dump (AbT), mobility and availability were assessed by selective extractions (water, ammonium nitrate salt solution, acetic acid, and oxalic-oxalate buffer). The results of the selective extraction procedure are shown in Fig. 3. Generally, the water-extractable forms ( $X_{w}$ ) constitute the readily soluble fraction (Sposito et al., 1982), forms extracted with ammonium nitrate salt solution ( $X_{am}$ ) are associated with the easily exchangeable and potentially bioavailable fraction (DIN 19730, 1995), the acetic acid extracts ( $X_{ac}$ ) represent the forms associated with carbonates and also cations specifically adsorbed by oxides as well as organic matter (Beckett, 1989), and the reducing oxalic-oxalate buffer form ( $X_{ox}$ ) represents the metal(-loid) fraction adsorbed to amorphous or poorly crystallized iron or manganese oxides (Schwertmann and Taylor, 1977).

Statistically significant differences ( $p < 0.05$ ) were found between the different selective extractions in the case of As, following the sequence  $As_{ox} \geq As_T > As_{ac} > As_{am} = As_w$ . Accordingly, most of the As (between 49.9–78.8% in relation to the total) was extracted by oxalic-oxalate buffer ( $As_{ox}$ ) with the highest proportion in the C layer of the AbT profile. Oxalic-oxalate buffer is the reagent that extracts specifically the elements adsorbed and retained by the thus dissolved Fe-Mn oxides. The results are consistent with previous observations (Aguilar et al., 2006; Martín et al., 2011) which found that As in polluted soils is associated mainly with iron oxides. Iron oxide phases are therefore generally accepted as the primary sorption sites for arsenic in many soils and sediments (Sadiq, 1997). Fe-Mn oxides are also important scavengers of heavy metals in soils, particularly in the high pH range (Li and Thornton, 2001). The residual fraction (extracted only with strong acids) is not as high (below 24% of the total) except in the B layer (mean 36% of the total), presumably associated with the presence of arsenopyrite in the tailings. Extractions determined that 6.5–13.3% of the total arsenic ( $As_T$ ) was extractable with acetic acid ( $As_{ac}$ ) without

**Table 2**

Mean and standard deviations ( $n = 3$ ) of general physicochemical properties of samples collected from vertical profile in the abandoned tailing dump (AbT). Letters (a, b) indicate significant differences between layers ( $p < 0.05$ ). EC: electrical conductivity; CEC: cation-exchange capacity; OC: organic carbon; AP: acid potential; NP: neutralization potential; NNP: net neutralization potential.

Area	Profile	pH	EC (dS/m)	CEC (cmol/kg)	CaCO <sub>3</sub> (%)	OC (%)	Clay (%)	Silt (%)	Sand (%)	AP kg/t	NP	NNP
AbT	A (0–30 cm)	8.1 ± 0.3 (a)	0.52 ± 0.57 (a)	6.1 ± 1.6 (a)	6.0 ± 2.5 (a)	0.37 ± 0.13 (a)	10.2 ± 2.5 (a)	25.7 ± 3.3 (a)	64.0 ± 0.8 (a)	20.3	15.5	−4.8
	B (30–80 cm)	8.2 ± 0.1 (a)	0.68 ± 0.39 (a)	4.9 ± 0.1 (a)	8.2 ± 3.2 (ab)	0.15 ± 0.06 (a)	9.2 ± 1.2 (a)	31.6 ± 4.1 (a)	59.3 ± 5.3 (a)	(±4.6)	(±2.9)	(±1.2)
	C (80–150 cm)	8.6 ± 0.1 (a)	0.29 ± 0.17 (a)	3.7 ± 0.3 (a)	14.4 ± 0.6 (b)	0.12 ± 0.05 (a)	8.3 ± 1.1 (a)	38.8 ± 4.7 (a)	52.8 ± 5.8 (a)			

**Table 3**

Total element concentrations in mg/kg<sup>-1</sup> (mean ± SD; n = 3) in the surface sampling (0–10 cm) at active (AcT) and abandoned (AbT) tailing dumps and in the vertical profile (AbT). Letters (a, b) indicate significant differences (p < 0.05); nd: not determined.

Area	Subarea	V	Cr	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
AcT	Soil	85.0 ± 12.7 (a)	46.5 ± 2.1 (a)	10.5 ± 2.1 (ab)	25.0 ± 2.8 (ab)	24.5 ± 0.7 (a)	84.0 ± 1.4 (a)	10.5 ± 2.1 (a)	1.3 ± 0.7 (a)	0.0 ± 0.0 (a)	36.0 ± 0.0 (a)
	Tailing	62.7 ± 2.5 (abc)	13.6 ± 1.5 (b)	9.0 ± 3.0 (ab)	5.7 ± 1.5 (a)	37.0 ± 9.8 (a)	233.7 ± 98.6 (a)	27.5 ± 5.0 (a)	1.0 ± 1.8 (a)	3.3 ± 0.6 (a)	137.3 ± 68.6 (a)
AbT	Soil (cover)	81.7 ± 4.9 (ab)	30.8 ± 13.5 (ab)	12.2 ± 1.5 (a)	15.0 ± 6.4 (ab)	29.5 ± 9.4 (a)	215.7 ± 109.4 (a)	132.2 ± 71.1 (a)	1.1 ± 1.0 (a)	7.5 ± 5.8 (a)	126.5 ± 123.3 (a)
Profile (AbT)	A	89.7 ± 14.5 (a)	35.9 ± 13.9 (ab)	11.1 ± 0.3 (a)	26.3 ± 12.1 (b)	23.97 ± 0.1 (a)	207.8 ± 91.6 (a)	1032.6 ± 928.8 (a)	2.4 ± 1.9 (a)	924.0 ± 824.7 (a)	246.3 ± 198.2 (a)
	B	47.5 ± 26.2 (bc)	29.3 ± 1.4 (ab)	7.0 ± 1.0 (ab)	16.2 ± 5.4 (ab)	42.4 ± 27.6 (a)	201.9 ± 29.4 (a)	385.3 ± 405.7 (a)	1.5 ± 0.7 (a)	362.1 ± 257.2 (a)	191.5 ± 5.5 (a)
	C	27.6 ± 1.0 (c)	15.3 ± 0.4 (b)	4.7 ± 0.6 (b)	11.8 ± 1.0 (ab)	38.4 ± 3.4 (a)	229.7 ± 38.9 (a)	347.2 ± 144.8 (a)	1.5 ± 0.3 (a)	68.1 ± 18.2 (a)	293.1 ± 103.3 (a)
Background		131	51	19	31	37	135	15	1	4	48
Interv. value (S) <sup>a</sup>		–	450	300	300	500	1000	50	10	–	500
Interv. value (D) <sup>b</sup>		250	380	240	210	190	720	55	12	15	530

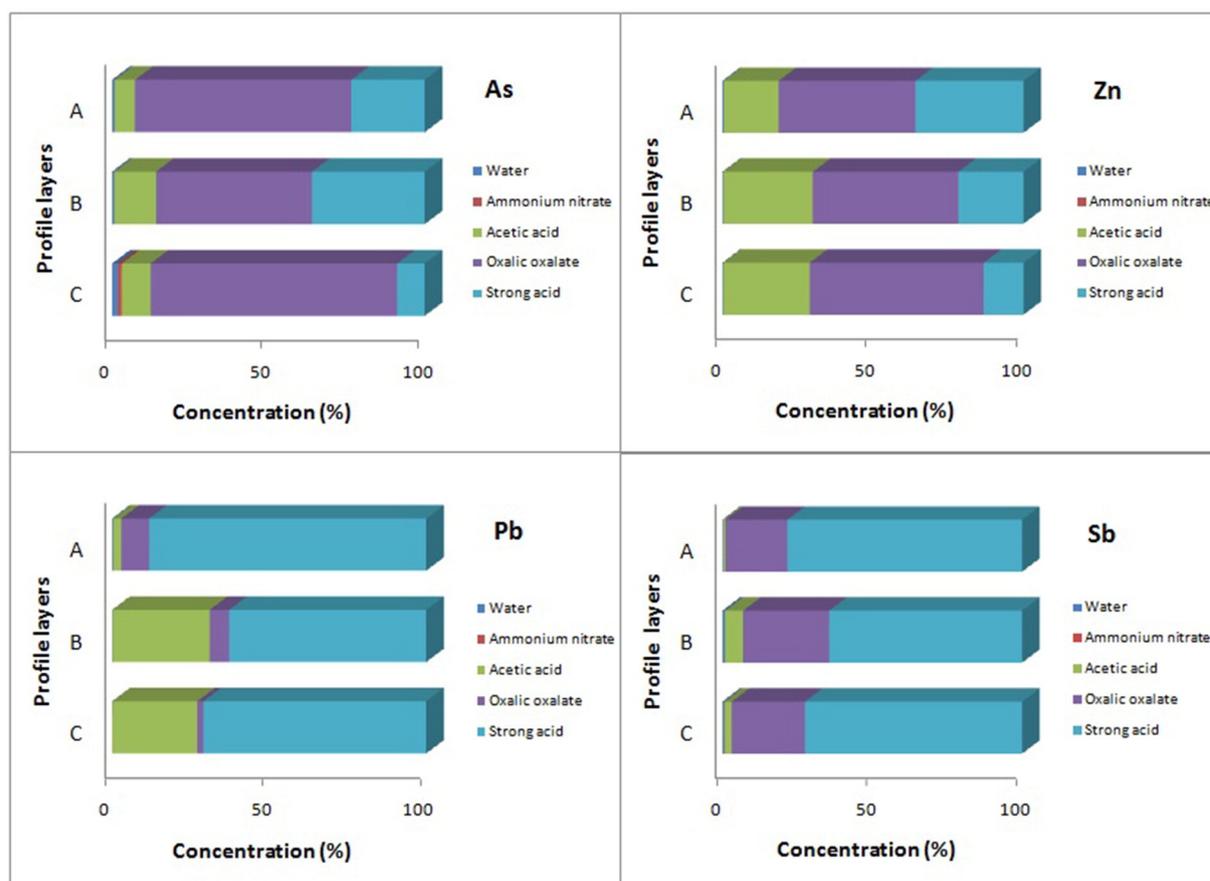
<sup>a</sup> Intervention value according to Ministry of Environment of the Board of Andalusia (Spain).

<sup>b</sup> Dutch Target and Intervention Values (The New Dutch List, 2000).

readsorption to other phases, whereas a negligible proportion (<2% of the total) was extracted by water ( $As_w$ ) and ammonium nitrate ( $As_{am}$ ). Low solubility and exchangeable potential of As measured by these extractants agree with the soil pH and the presence of carbonates (Rodrigues et al., 2010), and can be related by the incorporation of As into the lattice structure of calcite as arsenite under alkaline pH (Di Benedetto et al., 2006; Alexandratos et al., 2007). In our case, the precipitation of Ca–Fe(III)–AsO<sub>4</sub> phases was detected by SEM imaging (Fig. 4), indicating the possible presence of yukonite-like phases previously reported in oxidized As-bearing ores (Gomez et al., 2010) and in tailings of a gold-mining operation in Nova Scotia, Canada (Walker et al.,

2009). Despite the low water-soluble ratios, concentrations of  $As_w$  (mean 4.34 mg soluble As per kg dry soil) far surpassed the critical level of 0.04 mg of soluble As per kg dry soil (Bohn et al., 1985), indicating a need for detailed ecotoxicological studies to prevent the risk of pollution to the environment and the nearby population.

As with As, statistically significant differences (p < 0.05) were found between the different selective extractions in the case of Zn, following the sequence  $Zn_{ox} = Zn_T > Zn_{ac} > Zn_{am} = Zn_w$ . The highest extraction of Zn was in C layer and associated with the Fe–Mn oxides (mean 45.4–57.7% in relation to the total Zn), while the residual fraction had a mean range between 13.2–35.8% with the highest amount in the A



**Fig. 3.** Percentage of extracted metal(loid)s (mean values; n = 3) in relation to the total concentration in the different layers at the abandoned tailing dump.

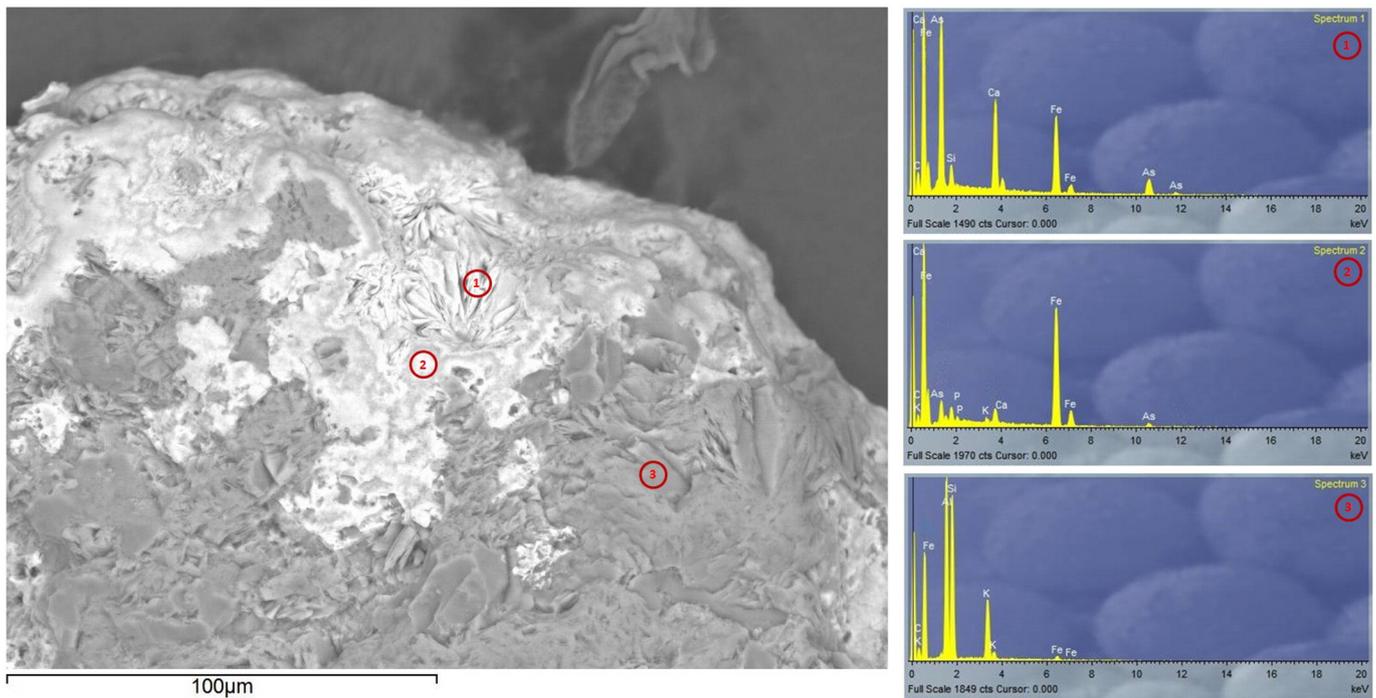


Fig. 4. Secondary precipitation of Ca-Fe(III)-AsO<sub>4</sub> phases (point 1) and amorphous Fe phases (point 2) on the surface of a grain of K-Fe aluminosilicate (point 3).

layer. These results agree with previous observations of Ashraf et al. (2012) and Li and Thornton (2001), who found that Zn was associated primarily with Fe/Mn oxides and the residual fraction. García et al. (2009) also stated that Zn may co-precipitate with oxides and hydroxides at high pH values. The next most abundant Zn fraction was that extracted with acetic acid (Zn<sub>ac</sub>), which accounted for a mean range of between 18.2–29.7% in relation to the total Zn; this fraction, also called the exchangeable fraction, registered the same percentage, according to Marguí et al. (2004), but in other studies even far higher percentages have been reported (Iavazzo et al., 2012), depending on the soil properties such as the Fe/Mn content. The percentage of the water-soluble (Zn<sub>w</sub>) and ammonium-nitrate-extracted (Zn<sub>am</sub>) fractions were negligible (mean < 0.5% for Zn<sub>w</sub> and below detection limit for Zn<sub>am</sub>). However, the mean value of water concentration of 0.6 mg soluble Zn per kg dry soil was within the toxic range (0.5 mg soluble Zn per kg dry soil) in soil solution reported by Ewers (1991), indicating a potential risk of environmental pollution for this element.

In the case of Sb, statistically significant differences ( $p < 0.05$ ) were found between the different selective extractions, following the sequence  $Sb_T \geq Sb_{ox} > Sb_{ac} > Sb_{am} = Sb_w$ . The highest concentration of Sb was in the residual fraction (mean 64.3–78.2% in relation to the total Sb), indicating that Sb is contained chiefly in the crystalline lattice of the secondary minerals. Wilson et al. (2010) reported that the residual Sb was up to 98% in mine-contaminated soils, but the relative proportion of Sb in this phase depends on the source (Tighe and Lockwood, 2007). The proportion of antimony extracted with oxalic-oxalate buffer (Sb<sub>ox</sub>) was below 30% of the total Sb, slightly below the values of the same extraction phase reported by Tighe and Lockwood (2007), where 30–47% of the total Sb was associated with non-crystalline Fe and Al hydroxides. The acetic-acid-soluble fraction (Sb<sub>ac</sub>) was low in relation to the total concentration (mean 0.7–5.9%), which coincides with the studies of He (2007) and Tighe and Lockwood (2007). The percentage of water-soluble (Sb<sub>w</sub>) and ammonium-nitrate-extracted (Sb<sub>am</sub>) in relation to the total Sb concentrations were very low (mean < 1%). Although Sb is generally described as a geochemically immobile element, its solubility depends on soil properties (Evangelou et al., 2012) and the rise of soil pH can inhibit Sb sorption to soil Fe

and Al oxy-hydroxides, increasing the Sb in soil-solution phase (Nakamaru et al., 2006).

Pb also presented statistically significant differences ( $p < 0.05$ ) between the different selective extractions, following the sequence  $Pb_T > Pb_{ac} = Pb_{ox} > As_{am} = As_w$ , indicating that this element was also associated mainly with the residual fraction (mean 70.9–88.2% in relation to the total Pb), containing the highest amount in the A layer. This agrees with the observations of Ashraf et al. (2012) and Ramirez et al. (2005), who reported that Pb is associated mostly with the residual phase. Pb associated with acetic acid-soluble fraction (Pb<sub>ac</sub>) accounted for mean 2.5–30.9% followed by a minor amount of oxalic-oxalate buffer-extractable fraction (mean 1.9–8.8% of the total). In this case, Pb is considered to be bound to carbonates and related to weathered (oxidized) precipitates from old tailing waste materials (Anju and Banerjee, 2010). The least abundant proportion of Pb was found in water-soluble (Pb<sub>w</sub> mean < 0.5%) and ammonium-nitrate-extracted (Pb<sub>am</sub> below the detection limit) fractions in relation to the total concentrations, with similar results as those observed by other authors (Ramos et al., 1994; Maiz et al., 2000). In any case, the Pb<sub>w</sub> concentrations did not exceed the toxic level in the soil solution (1 mg/kg) reported by Ewers (1991).

### 3.4. Correlation between tailing properties and metal(loid)s

Table 4 presents the correlation between the tailing properties and the total forms of metal(loid)s and forms that are water soluble and extractable by ammonium nitrate, acetic acid, and oxalic oxalate buffer. The results for arsenic indicate that As<sub>T</sub> together with As<sub>ac</sub> and As<sub>ox</sub> showed a significant ( $p < 0.05$ ) negative correlation with pH, indicating that for this type of pollution involving the release of sulphide tailings, their oxidation and hence acidification processes are related to the increase in total pollution by the generation of acidic conditions that lead to a release of contaminants (Romero-Freire et al., 2015; Simón et al., 2001). Significant correlation of As<sub>ac</sub> and As<sub>ox</sub> was found with OC in our samples. The effect of organic carbon to arsenic mobility is controversial. In some studies the application of organic matter reduced the As mobility (Gadepalle et al., 2007), whereas in others As is

**Table 4**

Pearson correlation between total (T), water soluble (w), ammonium nitrate (am), acetic acid (ac) and oxalic-oxalate (ox) extracted forms of As, Sb, Zn, Pb and tailing properties in the vertical profile of the abandoned tailing dump.

	AsT	As w	As am	As ac	As ox	SbT	Sb w	Sb am	Sb ac	Sb ox	ZnT	Zn w	Zn am	Zn ac	Zn ox	PbT	Pb w	Pb am	Pb ac	Pb ox
pH	−0.567 <sup>a</sup>			−0.893 <sup>a</sup>	−0.903 <sup>a</sup>	−0.650 <sup>a</sup>				−0.900 <sup>a</sup>						−0.595 <sup>a</sup>				−0.952 <sup>b</sup>
EC											0.575 <sup>a</sup>									
CEC											−0.818 <sup>b</sup>					−0.583 <sup>a</sup>	0.724 <sup>a</sup>			
CaCO <sub>3</sub>																			0.814 <sup>a</sup>	
OC	−0.550 <sup>a</sup>			0.880 <sup>a</sup>	0.899 <sup>a</sup>	−0.688 <sup>b</sup>				0.894 <sup>a</sup>										0.881 <sup>a</sup>
Clay											−0.602 <sup>a</sup>					−0.601 <sup>a</sup>				
Silt																				
Sand					0.870 <sup>a</sup>															
					−0.903 <sup>a</sup>															

<sup>a</sup> Correlation is significant at the 0.05 level (2-tailed).

<sup>b</sup> Correlation is significant at the 0.01 level (2-tailed).

mobilized after compost application and by phytoremediation due to the competing effect of organic matter with arsenate for adsorbing surface sites (Clemente et al., 2008; Martín et al., 2011). No correlation in relation to tailing properties was found for the As<sub>w</sub>, whereas a significant positive correlation was found for As<sub>am</sub> with silt fraction and a significant negative correlation with sand. Simón et al. (2001) showed that there was a strong positive correlation between arsenic levels and the fine-silt fraction of the sludge due to the enhanced specific surface available for As exchange.

In relation to the tailing properties, total (Sb<sub>T</sub>) and oxalic-oxalate buffer (Sb<sub>ox</sub>) showed similar behavior with As, presenting significant negative correlation with pH and OC. The oxyanion-forming metalloids As and Sb have comparable geochemical activity (Fu et al., 2016; Wilson et al., 2010). However, the understanding of Sb toxicity and environmental activity is limited (Filella et al., 2002). The other extracted forms of the Sb did not present any correlation with tailing properties, suggesting that these parameters do not control the partitioning of this metalloid.

By contrast, the correlation of tailing properties and Zn<sub>T</sub> showed significant positive correlation with electrical conductivity, indicating that Zn is strongly related to the soluble salts produced after the oxidation reactions (Romero-Freire et al., 2015). On the other hand, Zn<sub>T</sub> negatively correlated with CEC and clay fraction, suggesting that these tailing properties also affect Zn activity. This is consistent with the data in the literature indicating also that clay and soil hydroxides can strongly adsorb Zn especially under alkaline conditions (Vandana et al., 2011). No significant correlation was found for other Zn extractions.

Total concentrations of Pb were significantly and negatively correlated with pH, as well as with CEC and the clay fraction, indicating that alkaline pH, CEC, and the clay fraction were the main factors controlling the mobility of lead. As pH rises, Pb becomes less soluble under oxidizing conditions (Vandana et al., 2011) due to the formation of insoluble salts mainly under the presence of carbonates (Razo et al., 2004). The water-soluble form (Pb<sub>w</sub>) was not related to any of the soil properties except for the CEC, with a significant and positive correlation, indicating the favourable effect of the adsorption processes for the retention of Pb. Acetic acid extractable Pb (Pb<sub>ac</sub>) presented a significant correlation with CaCO<sub>3</sub> concentrations, while the proportion extracted by oxalic-oxalate buffer (Pb<sub>ox</sub>) significantly correlated with OC, indicating also a major contribution of OC in retaining Pb.

The mobility and potential toxicity were assessed in relation to physico-chemical properties of the tailings, using a principal-component analysis between total and soluble concentrations of the main pollutants and the tailing properties (Table 5). Three components explained 91.6% of the variance, with Component 1 being the one that included the total concentrations of metal(loid)s directly related to EC and inversely related to pH and CaCO<sub>3</sub>, indicating that the pollution is controlled fundamentally by tailing oxidation processes involving acidification, weathering of CaCO<sub>3</sub>, and increase in soluble salts (Simón et al., 2001). Component 2 includes the total concentrations of Zn and Pb inversely related to Zn<sub>w</sub> and Pb<sub>w</sub> forms, indicating that the soluble

forms of these elements are not controlled by their total concentrations, but rather that the CEC and texture (clay fraction) were the main properties affecting the water concentration of these elements in the soil solution (Kumpiene et al., 2008). Component 3, explaining the 20.9% of the variance, includes As<sub>w</sub> and Sb<sub>w</sub> forms inversely related to each other, indicating a contrasting relation between the two elements (Mitsunobu et al., 2006) and a strong influence of carbonates usually found in the silt fraction on the activity of the soluble forms of these elements, as reported by Martínez-Lladó et al. (2011).

The mobilization of pollutants in soils and tailings is strongly controlled by the presence of calcium carbonate and sulphide minerals. Our results indicate that the net neutralization potential (NNP) for the active tailing dump (AcT) potentially generates acid, so that long-term oxidation processes pose a potential hazard to the environment. In this sense, soils contaminated by heavy metals after sulfur oxidation are usually amended with calcium carbonate, but in some cases the amount of CaCO<sub>3</sub> required to neutralize acidity is underestimated. Long-term acidification over time was described after the liming of a soil polluted with heavy metals and small amounts of S (≈0.5%) (McTee et al., 2017), the formation of coatings around calcium carbonate grains being one of the main processes responsible for this underestimation and for the progress of acidification over time (Simón et al., 2005). Moreover, the transfer of heavy metals to plants in carbonate soils contaminated by mine tailings with high concentrations in heavy metals were reported in relation to local acidification and/or oxidation processes occurring in the rhizosphere (Boussen et al., 2013). Our data indicate that there is a potential risk of acidification and, therefore, of

**Table 5**

Principal-component analysis between total (X<sub>T</sub>) and soluble in water (X<sub>w</sub>) pollutant concentrations and main properties of the tailings.

	Rotated component		
	1	2	3
Zn <sub>T</sub>	0.504	−0.785	
As <sub>T</sub>	0.950		
Sb <sub>T</sub>	0.953		
Pb <sub>T</sub>	0.515	−0.738	
Zn <sub>w</sub>		0.960	
As <sub>w</sub>			0.940
Sb <sub>w</sub>			−0.858
Pb <sub>w</sub>		0.948	
pH	−0.862		
EC	0.751		
CEC		0.902	
CaCO <sub>3</sub>	−0.849		
OC	0.951		
Clay		0.879	
Silt		−0.685	0.632
Sand			−0.754
% cum. var.	35.4	70.7	91.6

Rotation method: Varimax with Kaiser Normalization. % cum. var.: Percentage of cumulative variance.

pollutant dispersion over time in the Chadak mining area that should be monitored and assessed with additional studies.

#### 4. Conclusion

Chadak ore field is one of the main gold-producing sites in Uzbekistan. Abandoned and active tailing dumps with wastes enriched with metal(loid)s poses a potential pollution risk for this mining area and for populations living in the vicinity. Our data indicate that the total concentrations of As, Sb, Zn, and Pb exceeded the background concentrations in wastes at the active tailing (ACT) dump and in soils at abandoned tailings dump (AbT). Waste deposits at AbT have very high concentrations of As (mean > 1030 mg/kg) and Sb (mean > 920 mg/kg), exceeding intervention threshold values by 20- and 62-fold, respectively. Selective extractions were made to assess the potential mobility and bioavailability of the pollutants both in wastes and in soils. Selective extraction results showed that As and Sb were strongly retained by iron oxides, but still with increased potential bioavailability (extractable with acetic acid); higher water-soluble and ammonium nitrate concentrations were also measured for both elements, indicating a potential toxicity risk for the environment. On the other hand, the selective extraction data showed that Zn and Pb were relatively immobile in the tailings, although in some cases large amounts of these elements were extracted with acetic acid, indicating a potential bioavailability once the neutralization potential is exceeded. However, a balance between the acid potential of the tailings and the neutralization potential indicate that the active tailing dump (ACT) is potentially acid generating, constituting a long-term hazard to the environment. Thus, more studies are required in the area for toxicity assessments using bioassays and for evaluations of the potential long-term risk of pollution in this area.

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#### References

Aguilar, J., Dorronsoro, C., Galán, E., Gómez, B.L., 1999. Criterios y estándares para declarar un suelo como contaminado en Andalucía. Public. Universidad de Sevilla (252 pp).

Aguilar, J., Dorronsoro, C., Fernández, E., Fernández, J., García, I., Martín, F., Sierra, M., Simón, M., 2006. Arsenic contamination in soils affected by a pyrite-mine spill (Aznalcóllar, SW Spain). *Water Air Soil Pollut.* 180, 271–281.

Alexandratos, V.G., Elzinga, E.J., Reeder, R.J., 2007. Arsenate uptake by calcite: macroscopic and spectroscopic characterization of adsorption and incorporation mechanisms. *Geochim. Cosmochim. Acta* 71, 4172–4187.

Anju, M., Banerjee, D.K., 2010. Comparison of two sequential extraction procedures for heavy metal partitioning in mine tailings. *Chemosphere* 78, 1393–1402.

Ashraf, M.A., Maah, M.J., Yusoff, I., 2012. Chemical speciation and potential mobility of heavy metals in the soil of former tin mining catchment. *Sci. World J.* 11 pages. <https://doi.org/10.1100/2012/125608>.

Astrom, M., 1998. Mobility of Al, Co, Cr, Cu, Fe, Mn, Ni and V in sulphide-bearing fine-grained sediments exposed to atmospheric O<sub>2</sub>: an experimental study. *Environ. Geol.* 36, 219–226.

Beckett, P.H.T., 1989. The use of extractants in studies on trace metals in soils, sewage sludge, and sludge-treated soils. In: Stewart, B.A. (Ed.), *Advances in Soil Science*, vol. 9. Springer-Verlag, New York, pp. 143–176.

Bohn, H.L., McNeal, B.L., O'Connor, G.A., 1985. *Soil Chemistry*. Wiley Interscience, New York, USA.

Boussen, S., Soubbrand, M., Bril, H., Ouerfelli, K., Abdeljaouad, S., 2013. Transfer of lead, zinc and cadmium from mine tailings to wheat (*Triticum aestivum*) in carbonated Mediterranean (Northern Tunisia) soils. *Geoderma* 192, 227–236.

Clemente, R., Dickinson, N.M., Lepp, N.W., 2008. Mobility of metals and metalloids in a multi-element contaminated soil 20 years after cessation of the pollution source activity. *Environ. Pollut.* 155, 254–261.

Dang, Z., Liu, C.Q., Martin, J.H., 2002. Mobility of heavy metals associated with the natural weathering of coal mine spoils. *Environ. Pollut.* 118, 419–426.

Di Benedetto, F., Costagliola, P., Benvenuti, M., Lattanzi, P., Romanelli, M., Tanelli, G., 2006. Arsenic incorporation in natural calcite lattice. Evidence from electron spin echo spectroscopy. *Earth Planet. Sci. Lett.* 246, 458–465.

DIN (Deutsches Institut für Normung Hrsg.) 19730, 1995. *Extraktion von Spurenelementen mit Ammoniumnitratlösung. Bodenbeschaffenheit*. Beuth Verlag, Berlin E DIN 19730.

Dudka, S., Adriano, D.C., 1997. Environmental impacts of metal ore mining and processing: a review. *J. Environ. Qual.* 26, 590–602.

Evangelou, M.W.H., Hockmann, K., Pokharel, R., Jakob, A., Schulin, R., 2012. Accumulation of Sb, Pb, Cu, Zn and Cd by various plants species on two different relocated military shooting range soils. *J. Environ. Manag.* 108, 102–107.

Ewers, W., 1991. Standards, guidelines and legislative regulatory concerning metals and their compounds. In: Merian, E. (Ed.), *Metals and Their Compounds in the Environment*. VCH Publishers, Weinheim, Germany, pp. 707–711.

Filella, M., Belzile, N., Chen, Y., 2002. Antimony in the environment: a review focused on natural waters I. Occurrence. *Earth-Sci. Rev.* 57, 125–176.

Filimonov, A.E., 2009. Environmental aspects of industry. *Gorniy Vestnik Uzbekistana*. 38, 98–101 (in Russian).

Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W., Giesy, J.P., 2016. Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China. *Sci. Total Environ.* 539, 97–104.

Gadepalle, V.P., Ouki, S.K., Van Herwijnen, R., Hutchings, T., 2007. Immobilization of heavy metals in soil using natural and waste materials for vegetation establishment on contaminated sites. *Soil Sediment Contam.* 16, 233–251.

García, I., Díez, M., Martín, F., Simón, M., Dorronsoro, C., 2009. Mobility of arsenic and heavy metals in a sandy-loam textured and carbonated soil. *Pedosphere* 19, 166–175.

Gleyzes, C., Tellier, S., Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *TrAC Trends Anal. Chem.* 21 (6–7), 451–467.

Gomez, M.A., Becze, L., Blyth, R.I.R., Cutler, J.N., Demopoulos, G.P., 2010. Molecular and structural investigation of yukonite (synthetic & natural) and its relation to arseniosiderite. *Geochim. Cosmochim. Acta* 74 (20), 5835–5851.

Hayes, S., Webb, S., Bargar, J., O'Day, P., Maier, R., Chorover, J., 2012. Geochemical weathering increases lead bioaccessibility in semi-arid mine tailings. *Environ. Sci. Technol.* 46, 5834–5841.

He, M., 2007. Distribution and phytoavailability of antimony at an antimony mining and smelting area, Hunan, China. *Environ. Geochem. Health* 29, 209–219.

Iavazzo, P., Adamo, P., Boni, M., Hillier, S., Zampella, M., 2012. Mineralogy and chemical forms of lead and zinc in abandoned mine wastes and soils: an example from Morocco. *J. Geochem. Explor.* 113, 56–67.

Jung, M.C., 2008. Heavy metal concentrations in soils and factors affecting metal uptake by plants in the vicinity of a Korean Cu-W mine. *Sensors* 8, 2413–2423.

Kempton, H., Atkins, D., 2000. Delayed environmental impacts from mining in semi-arid climates. Proceedings from the 5th International Conference on Acid Rock Drainage ICARD 2000. Society for Mining Metallurgy and Exploration, Inc., Denver, CO, U.S.A., pp. 1299–1308 May 2000.

Kersten, M., 2001. Speciation of trace metals in sediments. In: Ure, A.M., Davidson, C.M. (Eds.), *Chemical Speciation in the Environment*, 2nd Ed Blackwell Science, Oxford, pp. 301–321.

Kuldashv, A.G., Abdurahmanov, A.A., 2009. Chadak deposits - firstborns of the gold industry of the Republic of Uzbekistan (in Russian). *Gorniy Vestnik Uzbekistana*. 38, 44–47.

Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments: a review. *Waste Manag.* 28, 215–225.

Lawrence, R.W., Scheske, M., 1997. A method to calculate the neutralization potential of mining wastes. *Environ. Geol.* 32, 100–106.

Li, X., Thornton, I., 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. *Appl. Geochem.* 16 (15), 1693–1706.

Lottermoser, B.D., 2010. *Mine Wastes. Characterization, Treatment and Environmental Impacts*. 3rd ed. Springer-Verlag Berlin Heidelberg (400 p).

Maiz, I., Arambarri, I., García, R., Millan, E., 2000. Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. *Environ. Pollut.* 110, 3–9.

MAPA, 1994. *Métodos Oficiales de Análisis*. Tomo III Secretaría General Técnica del Ministerio de Agricultura, Pesca y Alimentación (MAPA), Madrid, Spain.

Marañes, C.A., Sánchez, G.J.A., De Haro, L.S., Sánchez, G.S.T., Del Moral, T.F., 1998. *Análisis de suelos: Metodología e interpretación* (Almería, España).

Marguí, E., Salvadó, V., Queralt, I., Hidalgo, M., 2004. Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes. *Anal. Chim. Acta* 524, 151–159.

Martín, F., Díez, M., García, I., Simón, M., Dorronsoro, C., Iriarte, A., Aguilar, J., 2007. Weathering of primary minerals and mobility of major elements in soils affected by an accidental spill of pyrite tailing. *Sci. Total Environ.* 378, 49–52.

Martín, F., Escoto, M., Fernández, J., Fernández, E., Arco, E., Sierra, M., Dorronsoro, C., 2010. Toxicity assessment of sediments with natural anomalous concentrations in heavy metals by the use of bioassay. *Int. J. Chem. Eng.*, 101390 <https://doi.org/10.1155/2010/101390>.

Martín, F., Simón, M., Arco, E., Romero, A., Dorronsoro, C., 2011. Arsenic behaviour in polluted soils after remediation activities. In: Hernandez-Soriano, M.C. (Ed.), *Soil Health and Land Use Management*. InTech, Rijeka, pp. 201–216.

Martín Peinado, F., Romero-Freire, A., García, I., Sierra, M., Ortiz, I., Simón, M., 2015. Long term contamination in a recovered area affected by mining spill. *Sci. Total Environ.* 514, 219–223.

Martínez-Lladó, X., Valderrama, C., Rovira, M., Martí, V., Giménez, J., de Pablo, J., 2011. Sorption and mobility of Sb(V) in calcareous soils of Catalonia (NE Spain): batch and column experiments. *Geoderma* 160, 468–476.

- Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background - can we calculate it? *Environ. Geol.* 39, 990–1000.
- McTee, M.R., Lekberg, Y., Bullington, L., Rummel, A., Mummy, D.L., Ramsey, P.W., Hinman, N.W., 2017. Restoring ecological properties of acidic soils contaminated with elemental sulfur. *Sci. Total Environ.* 587–588, 449–456.
- Mitsunobu, S., Harada, T., Takahashi, Y., 2006. Comparison of antimony behavior with that of arsenic under various soil redox conditions. *Environ. Sci. Technol.* 40, 7270–7276.
- Nakamaru, Y., Tagami, K., Uchida, S., 2006. Antimony mobility in Japanese agricultural soils and the factors affecting antimony sorption behavior. *Environ. Pollut.* 141, 321–326.
- Nriagu, J.O., Bhattacharya, P., Mukherjee, A.B., Bundschuh, J., Zevenhoven, R., Loeppert, R.H., 2007. Arsenic in soil and groundwater: an introduction. In: Bhattacharya, P., Mukherjee, A.B., Bundschuh, J., Zevenhoven, R., Loeppert, R.H. (Eds.), *Arsenic in Soil and Groundwater Environment: Biogeochemical, Interactions, Health Effects and Remediation. Trace Metals and Other Contaminants in the Environment*. vol. 9. Elsevier, Amsterdam, pp. 1–58.
- Nyamangara, J., 1998. Use of sequential extraction to evaluate zinc and copper in a soil amended with sewage sludge and inorganic metal salts. *Agric. Ecosyst. Environ.* 69, 135–141.
- Quevauviller, Ph., 2002. Operationally defined extraction procedure for soil and sediment analysis. Part 3: new CRMs for trace-element extractable contents. *Trends Anal. Chem.* 21, 774–785.
- Ramirez, Marco, Massolo, Serena, Frache, Roberto, Correa, Juan A., 2005. Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile. *Mar. Pollut. Bull.* 50, 62–72.
- Ramos, L., Hernandez, L.M., Gonzales, M.J., 1994. Sequential fractionation of copper, lead, cadmium and zinc in soil from or near Doñana national park. *J. Environ. Qual.* 23, 50–57.
- Rauret, G., Rubio, R., López-Sánchez, J.F., 1989. Optimization of Tessier procedure for metal solid speciation in river-sediments. *Int. Environ. Anal. Chem.* 36, 69–83.
- Razo, I., Carrizales, L., Castro, J., Díaz-Barriga, F., Monroy, M., 2004. Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. *Water Air Soil Pollut.* 152, 129–152.
- RIVM (National Institute for Public Health and Environmental Protection), 2000. Annex A: Target Values, Soil Remediation Intervention Values and Indicative Levels for Serious Contamination, Dutch Target and Intervention Values, (the New Dutch List), Netherlands.
- Rodrigues, S.M., Henriques, B., Coimbra, J., Ferreira da Silva, E., Pereira, M.E., Duarte, C., 2010. Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils. *Chemosphere* 78, 1301–1312.
- Romero-Freire, A., Sierra-Aragón, M., Ortiz-Bernad, I., Martín-Peinado, F., 2014. Toxicity of arsenic in relation to soil properties: implications to regulatory purposes. *J. Soils Sediments* 14, 968–979.
- Romero-Freire, A., García, I., Simón, M., Martínez, F.J., Martín, F., 2015. Long-term toxicity assessment of soils in a recovered area affected by a mining spill. *Environ. Pollut.* 208, 553–561.
- Sadiq, M., 1997. Arsenic chemistry in soils: an overview of thermo-dynamic predictions and field observations. *Water Air Soil Pollut.* 93, 117–136.
- Sánchez-Marañón, M., Romero-Freire, A., Martín-Peinado, F.J., 2015. Soil-color changes by sulfuric acid induced from a pyritic surface sediment. *Catena* 135, 173–183.
- Sauve, S., Hendershot, W., Allen, W.E., 2000. Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environ. Sci. Technol.* 34, 1125–1131.
- Schwertmann, U., Taylor, R.M., 1977. Iron oxides. In: Dixon, J.B., Webb, S.B. (Eds.), *Minerals in Soil Environments*. Soil Science Society of America, Madison, WI, pp. 148–180.
- Sheppard, S.C., Sheppard, M.I., Sanipelli, B., Gallerand, M.O., Long, J., 2005. Ecotoxicological probable-no-effect concentrations for elements related to nuclear waste. *Australas. J. Ecotoxicol.* 11, 115–136.
- Shukurov, N., Kodirov, O., Peitzsch, M., Kersten, M., Pen-Mouratov, S., Steinberger, Y., 2014. Coupling geochemical, mineralogical and microbiological approaches to assess the health of contaminated soil around the Almayk mining and smelter complex, Uzbekistan. *Sci. Total Environ.* 476–477, 447–459.
- Simón, M., Martín, F., Ortiz, I., García, I., Fernández, J., Fernández, E., Dorronsoro, C., Aguilar, J., 2001. Soil pollution by oxidation of tailings from toxic spill of a pyrite mine. *Sci. Total Environ.* 279, 63–74.
- Simón, M., Martín, F., García, I., Bouza, P., Dorronsoro, C., Aguilar, J., 2005. Interaction of limestone grains and acidic solutions from the oxidation of pyrite tailings. *Environ. Pollut.* 135, 65–72.
- Smirnova, S.K., Shamaev, O.T., 2012. The Fergana valley. *Geology and mineralogy. Geosciences in Uzbekistan*. SE “SMIMR”, Tashkent, pp. 141–145.
- Smirnova, S.K., Kozlov, V.V., Shamaev, O.T., Ignatkov, E.N., 2009. The manner of occurrence of some elements (Au, Ag, Pt, Se, Te, Hg) at epithermal gold-silver deposit Western Chadak (Uzbekistan, Kurama ridge). IX International Conference “New Ideas in Earth Sciences”. 230 Moscow.
- Sposito, G., Lund, L.J., Chang, A.C., 1982. Trace metal chemistry in arid-zone field soils amended with sewage sludge. I: fractionation of Ni, Cu, Zn, Cd and Pb in solid phases. *Soil Sci. Soc. Am. J.* 46, 260–264.
- SRK, 1989. Draft Acid Rock Drainage Technical Guide. Prepared by Steffen, Robertson and Kirsten Inc. in association with Norecol Environmental Consultants and Gormely Process Engineering. Technical Guide, Vancouver, Canada. <http://www.empr.gov.bc.ca/Mining/Geoscience/PublicationsCatalogue/MiscellaneousPublications/Documents/DraftAcidRockDrainageTechGuideVol.1.pdf>.
- SSDS (Soil Survey Division Staff), 1993. Soil survey manual. Soil conservation service. US Department of Agriculture Handbook. vol. 18. US Department of Agriculture, Washington, DC.
- Tighe, M., Lockwood, P., 2007. The importance of non-crystalline hydroxide phases in sequential extractions to fractionate antimony in acid soils. *Commun. Soil Sci. Plant Anal.* 38, 1487–1501.
- Ure, A.M., Quevauviller, Ph., Muntau, H., Griepink, B., 1993. Speciation of heavy metal in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.* 51, 135–151.
- Van den Berg, R., Dennenman, C.A., Roels, J.M., 1993. Risk assessment of contaminated soil: proposal for adjusted, toxicologically based Dutch soil clean-up criteria. In: Arendt, F., Annokke, G.J., Bosman, R., van der Brink, W.J. (Eds.), *Contaminated Soils '93*. Kluwer Academic Publisher, London, pp. 349–364.
- Vandana, P., Murthy, N.N., Praveen, R.S., 2011. Assessment of heavy metal contamination in soil around hazardous waste disposal sites in Hyderabad city (India): natural and anthropogenic implications. *E3. J. Environ. Res. Manag.* 2 (2), 27–34.
- Walker, S.R., Parsons, M.B., Jamieson, H.E., Lanzirotti, A., 2009. Arsenic mineralogy of near-surface tailings and soils: influences on arsenic mobility and bioaccessibility in the Nova Scotia gold mining districts. *Can. Mineral.* 47, 533–556.
- Wilson, S.C., Lockwood, P.V., Ashley, P.M., Tighe, M., 2010. The chemistry and behavior of antimony in the soil environment with comparisons to arsenic: a critical review. *Environ. Pollut.* 158, 1169–1181.