



## Understanding Copper speciation and mobilization in soils and mine tailings from “Mineral La Aurora” in central Mexico: contributions from Synchrotron techniques

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### Abstract

Potentially toxic elements are usually present in mine tailings in concentrations that may threaten environmental and human health. In this research, mine tailings and soils from the mine "La Aurora" located in central Mexico were studied. This mine was exploited for Pb, Zn, Ag, Cu and Au and abandoned since their last cycle in 1957. For this purpose, a combination of sequential extraction procedure (SEP), Flame Atomic Absorption Spectroscopy (FAAS), and X-ray synchrotron techniques (XAS) were used. Cu is present in mine tailings and soils in a range respectively between  $125 \pm 21$  and  $1763 \pm 10 \text{ mg} \cdot \text{kg}^{-1}$  and  $22 \pm 2$  and  $88 \pm 5 \text{ mg} \cdot \text{kg}^{-1}$ . Repartition of Cu in mine tailings determined by SEP followed this general trend: Water soluble > Residual > Organic Bound > Exchangeable > Fe-Mn oxides bound > Carbonates bound. In contrast, Cu in soils was mainly retained in the residual fraction and followed this general trend: Residual > Organic bound > Fe-Mn oxides bound > Carbonates bound > Water soluble > Exchangeable. X-ray Absorption Near Edge Spectroscopy (XANES), showed that Cu is present as  $\text{Cu}^{2+}$ , forming highly mobile species, and in minor proportion as  $\text{Cu}^+$  species, as oxides and sulphides. Cu content in mine tailings is available for plants and bioaccessible with percentages higher than 50 % in almost all the points tested. The calculated dose limit, that involves gastrointestinal disorders for chronic exposure is surpassed in all mine tailings tested.

Keywords: Copper, mine tailings, X-ray absorption spectroscopy.

### Resumen

*La concentración de Elementos Potencialmente Tóxicos en desechos mineros suele ser muy alta, en concentraciones que pueden constituir un riesgo para el medio y la salud humana. En este trabajo, se estudiaron jales y suelos del sitio de la mina “La Aurora”, localizado en la región central de México. Este sitio minero fue explotado para Pb, Zn, Ag, Cu y Au y abandonado desde su último ciclo en 1957. Con este propósito se empleó una combinación de Extracciones Secuenciales, Espectroscopía de Absorción Atómica de Flama y Técnicas de Luz Sincrotrón. La concentración de Cu determinada en los jales y suelos se encontró respectivamente en un rango de  $125 \pm 21$  and  $1763 \pm 10 \text{ mg} \cdot \text{kg}^{-1}$  y  $22 \pm 2$  a  $88 \pm 5 \text{ mg} \cdot \text{kg}^{-1}$ . La distribución de Cu en los jales determinada por las Extracciones Secuenciales presentó la siguiente tendencia: Soluble en agua > Residual > Unido a materia orgánica > Intercambiable > Unido a óxidos de Fe-Mn > Unido a carbonatos. En contraste, el Cu en el suelo es retenido principalmente en la fracción residual, como sigue: Residual > Unido a materia orgánica > Unido a óxidos de Fe-Mn > Unido a Carbonatos > Soluble en agua > Intercambiable.*

*Los estudios de Espectroscopia de Absorción de rayos X cerca de la Estructura del Borde, mostraron que el Cu se encuentra presente formando especies altamente solubles de  $\text{Cu}^{2+}$  y en menor proporción como óxidos y sulfuros de  $\text{Cu}^+$ . El Cu contenido en los jales se encuentra bioaccesible y disponible para las plantas, con porcentajes de mas del 50 % en casi todos los puntos estudiados. Todos los jales muestreados superan el límite de la dosis calculada que involucra desordenes gastrointestinales por exposición crónica.*

*Palabras clave: Cobre, residuos mineros, espectroscopia de absorción de rayos X.*

## 1. Introduction

Mine tailings are source of heavy metal pollution around the world and their residues constitute a risk for environmental and human health since they usually display elevated concentrations of Potentially Toxic Elements (PTE). The exposure of living organisms to these types of residues may result in physiological damage, risking their wellbeing. In the case of Cu, which is in the focus of this study, high doses ( $0.0731 \text{ mg}\cdot\text{kg}\cdot\text{day}^{-1}$ ) in humans may induce gastrointestinal irritation and in some cases liver damage (ATSDR, 2004). Cu is also indirectly associated with a number of neurological disorders, including Alzheimer's and prion disease (Stern *et al.*, 2007). In addition, it participates in cellular damage via oxidation by cupric ion (Freedman *et al.*, 1986). In plants, Cu may cause morphological and physiological disorders including growth decrease and effects in photosynthetic activity. According to Mohanty *et al.* (1989), Cu acts as a potent inhibitor of photosynthetic electron transport at concentrations  $\geq 0.06 \text{ mg L}^{-1}$  in soil solution. The critical range for toxicity in leaves are between  $20 - 30 \text{ mg}\cdot\text{kg}^{-1}$  for crop species and around  $18 \text{ mg}\cdot\text{kg}^{-1}$  for grass species (Plenderleith and Bell, 1990; Alaoui-Sossé *et al.*, 2004). In addition, plants, as the basis of food chain, could contribute to mobilize Cu and other PTE present in soils and waters (Ryan *et al.*, 2013). In this context, mobilization is dependent on elemental speciation and the nature of the media containing the pollutant.

Reports on Cu levels in mine tailings vary significantly around the world. For example, in China and Zambia, Cu concentrations between  $455$  to  $9979 \text{ mg}\cdot\text{kg}^{-1}$  have been reported (Sracek *et al.*, 2010; Zebo *et al.*, 2012; Yao-Guang *et al.*, 2013). The mobilization of PTE from mine tailing zones to surrounding soils represents a threat for the local environment. For example, Montenegro *et al.* (2009) found Cu levels around  $375.1 \text{ mg}\cdot\text{kg}^{-1}$ , in soils near the Chilean Cu mine tailings of "La Cocinera". Cu content in soils exceeding  $200 \text{ mg}\cdot\text{kg}^{-1}$  are considered as anomalous (Bowie and Thorton, 1985). Regulations for Cu in soils are between  $50$  (Holland) to  $1000 \text{ mg}\cdot\text{kg}^{-1}$  (Spain) (Belmonte Serrato *et al.*, 2010).

Mine tailings have been studied for environmental purposes with the use of physical methods such as Scanning Electron Microscopy (SEM), X-ray Fluorescence (XRF), and XAS. Yang *et al.* (2014) used XANES, Extended X-ray Absorption Fine Structure (EXAFS), micro X-ray

Fluorescence ( $\mu$ -XRF) spectroscopy and Scanning Transmission X-ray Microscopy (STXM) to investigate speciation and distribution of Cu in mine tailings from Zhuji Country of Zhejiang province, China. Their results suggest that Cu is associated with Fe oxides, adsorbed to Fe(III) oxides by inner-sphere complexation. Mamindy-Pajany *et al.* (2014) used micro X-ray Absorption Near Edge Structure ( $\mu$ -XANES) and  $\mu$ XRF spectroscopy to investigate the spatial distribution of Ca, Fe, Ni, Cu and Zn, in a biosolid-amended soil. They concluded that there Cu have a close relation with Fe oxy (hydr) oxides. Donner *et al.* (2011) also used XRF and XAS techniques to investigate the speciation of Cu and Zn in bio solids from Australia; they improved a combination of XANES, EXAFS and  $\mu$ -XRF imaging to understand elemental associations within bio solids. Their results suggest that Cu and Zn are closely associated with Fe and this is one of the mechanisms controlling their mobility. For a better understanding of Cu mobility and speciation it is necessary to perform experiments about bioaccessibility and phytoaccessibility in order to get information of Cu fractions susceptible of entering in to the food chain. In this work, we combined spectroscopic techniques and extractions procedures to elucidate the speciation of Cu in mine tailings and its mobilization to the near environment of the abandoned mine "La Aurora".

## 2. Work area description

The site of study is called "La Aurora" and is located  $4 \text{ km}$  NW of Xichú town, in Guanajuato, Mexico,  $393071 \text{ m N}$  and  $2359296 \text{ m W}$  (UTM). This zone belongs to a natural protected area called "Sierra Gorda" with high biodiversity of species and biological resources. Located at the central zone of the folded belt of Jurassic and Cretaceous carbonate rocks, elevations are between  $900$  to  $2400 \text{ masl}$ . The weather is semi arid with summer rains, and temperatures range between  $18$  to  $22 \text{ }^\circ\text{C}$ . The Mine "La Aurora" was exploited for Pb, Zn, Ag, Cu and Au, and is abandoned since 1957 (SEMARNAT, 2005; Carrillo-Chávez *et al.*, 2014).

## 3. Methods

### 3.1. Mine tailing and soil sampling

Samples of mine tailings were collected from 13

sampling points, distributed over the mine tailing area and five points in soils located near the end of the mine tailings. Three more points were sampled in soils located at a distance of 1.5 km from the wastes as controls. Composites samples were taken at 1 and 30 cm depth per sampling point, except in soils where all samples are composites of 30 cm depth. Samples were dried at 50 °C for 24 h and sieved in two particle sizes: < 0.25, < 0.85 mm (mesh 60 and 20), according to the Mexican regulations for metal content determination in soils for remediation (NOM-147-SEMARNAT/SSA1, 2007), and EPA method 3050b (US-EPA, 1996) for acid digestion of sediments, sludge and soils. All samples were transferred to the Toxicology Laboratory at the University of Guanajuato for analysis of metal contents and for different extraction procedures to get information, for example about bio and phytoaccessibility. In soil samples, pH values ranged 7.3 – 8.2 and, in mine tailings, 2.8 – 6.6. Additionally,  $\mu$ -XRF and  $\mu$ -XANES spectra have been measured using synchrotron radiation, due to limited amount of beamtime, this manuscript presents results from two mine tailing samples and one soil only.

### 3.2. Total Cu content analysis

Mine tailings and soil samples were analyzed using FAAS and XRF (only in selected samples for validation purposes) for total Cu content. For FAAS analysis, tailings and soil samples were digested under reflux according 3050b EPA method (US-EPA, 1996). 1 g of sample was weighed in a 50 mL polypropylene centrifuge tube and then 5 mL of HNO<sub>3</sub> (Reagent grade, Fermont) were added. Mixtures were boiled for about 1 h with a reflux condenser. Later, 3 mL of H<sub>2</sub>O<sub>2</sub> (30 %; Fermont) were added before boiling continued for about 1 h more. The residue was centrifuged at 3000 x g and filtered with a 2.5  $\mu$ m membrane (Whatman ©), gauged to 10 mL of deionized water in a volumetric flask and stored at 4 °C in centrifuge tubes until analysis. FAAS analysis was carried out by flame technique at 324.8 nm with a lamp current of 4.0 mA and slit of 0.5 nm in a PerkinElmer HGA 800 and SpectrAA 220FS.

For XRF analysis 100 to 300 mg of the powdered samples were pressed into pellets using a pellet die and hydraulic press. <sup>109</sup>Cd (25 mCi) (Isotope Products Laboratories, Valencia, USA) was used as the primary excitation sources for the analysis. The fluorescence radiation emitted was collected using an energy dispersive X-ray spectrometer, equipped with a Si (Li) detector (Canberra, 157 Meriden, USA), with a 25- $\mu$ m-thick Be window. The XRF analysis was performed in air, and the samples were irradiated for 1000 to 5000 s to obtain spectra with sufficient statistics (Necemer *et al.*, 2008). X-ray fluorescence spectra were analyzed with the iterative least squares programme (AXIL) (Van-Grieken, 1993), as included in the quantitative X-ray analysis system software package (Vekemans *et al.*, 1994). Element quantification from the measured spectra was performed using the quantitative analysis of environmental

samples based on fundamental parameters (IAEA, 2011). Quality assurance for the element analyses was performed using as standard reference material 2730a Montana Soil.

### 3.3. Extraction procedures

For chemical extraction procedures 4 mine tailing (T1, T2, T10, T12), 2 soil (S1, S2) and one reference (S1R) site samples were selected. Extractions were performed in composite and surface samples from both particle size fractions < 0.25, < 0.85 mm (mesh 60 and 20). Bioaccessibility was determined only in the particle size < 0.25 mm fraction (mesh 60), since this is the representative fraction of solids that may adhere to the hands of children and prone to be swallowed.

#### 3.3.1. Bioaccessibility

Bioaccessibility was determined by quantifying the fraction of Cu that is soluble in a gastric media. This provides a measure of the oral exposure of Cu. Gastric media extraction was performed according to the Mexican Regulation (NOM-147-SEMARNAT-SSA1, 2007). Gastric media was simulated by a solution of 0.4 M Glycine (Reagent plus; Ultra Sigma), acidified with HCl at pH 1.5  $\pm$  0.05 (reagent grade; Fermont). 1g of sample was weighed in a 1 L glass recipient in triplicate and then 100 mL of gastric media were added. Solutions were shaken at 30  $\pm$  2 rpm at 37 °C for 1 h. After this, 20 mL of extract were centrifuged at 3000 x g and filtered with a 2.5  $\mu$ m membrane (Wathman ©) and stored at 4 °C until analysis with FAAS. We calculated the estimated dose for oral exposition in children, in order to establish the potential toxicity via soil ingestion. Data used for this purpose were taken of similar studies in the same region (central Mexico area); using a soil ingest of 200 mg-day<sup>-1</sup>, 52 h of exposition and 52 kg weight for a child between 6 and 9 years (CEPIS, 1998).

#### 3.3.2. Phytoaccessibility

Phytoaccessibility was determined by extraction with a solution of Low Weight Molecular Organic Acids (LWMOA), simulating a chemical rhizosphere environment. Organic acids control the solubility of some elements and therefore the possibility to get into the plant tissue. Composition of solution was described by Cieřliński *et al.* (1998): acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>; 2898 mM), succinic (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>; 194 mM), oxalic (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; 43 mM), malic (C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>; 39.8 mM), tartaric (C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>; 26.3 mM), fumaric (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>; 12 mM) and citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>; 6 mM). Extraction was performed using 1 g of sample and the LWMOA solution in a 1:15 proportion (pH 4.5  $\pm$  0.1). Solutions were shaken for 5 h, centrifuged at 3000 x g, filtered with a 2.5  $\mu$  membrane (Whatman©), and stored at 4 °C until analysis by FAAS.

#### 3.3.3. Sequential Extraction Procedure

Sequential extraction used for this purpose was a modified version of Tessier *et al.* (1979) for the speciation of

particulate trace metals. 1 g of each sample was weighed and stored in a 50 mL centrifuge tube by triplicate. Extraction was performed as follows: 1) Water soluble, 15 mL of deionized water was added and stirred for 2 h at room temperature; 2) Exchangeable, 8 mL of 1M MgCl<sub>2</sub> (pH 7.0) were added to the solid residue from the previous step, and stirred for 1h at room temperature; 3) Carbonates bound, 8 mL of 1M NaOAc (pH 5.0 with HOAc) were added to the solid residue from the previous step, and stirred for 5 h at room temperature; 4) Fe-Mn oxides bound, 15 mL of 0.04 M NH<sub>2</sub>OH·HCL in 25 % (v/v) HOAc were added to the solid residue from the previous step, during 6 h at 96 °C with occasional stirring; 5) Organic bound, 3 mL of 0.02 M HNO<sub>3</sub> and 5 mL of 30 % H<sub>2</sub>O<sub>2</sub> (pH 2 with HNO<sub>3</sub>), heated during 2 h at 85 °C with occasional stirring, after that another 3 mL of H<sub>2</sub>O<sub>2</sub> (pH 2 with HNO<sub>3</sub>) was added, heated during 3 h at 85 °C with occasional stirring; 6) Residual was extracted with acid extraction with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. After each step solid residue was washed with 15 mL of deionized water, centrifuged at 3000 x g, filtered with a 2.5 μ membrane (Wathman ©), and stored at 4 °C until analysis by FAAS.

### 3.4. Synchrotron analysis

Synchrotron analyses were performed for two mine tailing (T1, T2) and one soil (S1) sample (surface and composite). Due to limited availability of beamtime preference was given to the particle size < 0.25 mm (mesh 60) fraction, which is the most prone to weathering processes.

#### 3.4.1. Bulk XAS

XAS measurements were performed at the XAFS beamline of the Elettra Sincrotrone Trieste. All samples were pulverized and homogenized using an agate mortar, mixed with Boron nitride or Polivinil Pirrolidone and prepared as pellets. References were mounted on adhesive tape. The following reference compounds and minerals were used to compare against unknown samples: clinoclase (Cu<sub>3</sub>AsO<sub>4</sub>(OH)<sub>3</sub>), copper(II) sulfate/chalcanthite (CuSO<sub>4</sub>·5H<sub>2</sub>O), copper(II) oxide (CuO), copper (I) oxide (Cu<sub>2</sub>O), olivenite (Cu<sub>2</sub>AsO<sub>4</sub>OH), and copper acetate Cu(CH<sub>3</sub>COO)<sub>2</sub>. Due to the high content of As we selected two of the most common copper arsenates found in oxidized zones of base metal deposits clinoclase and olivenite (Anthony *et al.*, 2003). The latter were obtained from Excalibur minerals, the other reference substances were purchased as reagent grade chemicals from sigma Aldrich. XANES data acquisition was performed with the use of a Silicon Drift Detector (SDD; KETEK GmbH AXAS-M with an assembled 80 mm<sup>2</sup> SDD) in fluorescence mode for diluted samples (soil), and in transmission mode for model compounds and samples with high Cu content. Cu K edge (8979 eV) was calibrated using a Cu<sup>0</sup>-foil and scanned 120 eV below the edge (5eV energy steps) and 220 eV above the edge (0.2 eV energy steps), energy was selected by a Si

(111) double crystal monochromator. Multiple scans (2 – 10) were collected and averaged for each sample in order to obtain adequate signal to noise. XANES data analysis was performed using Athena (Ravel and Newville, 2005) programs. Normalized data was used for XANES and Linear Combination Fits (LCF). LCF were performed in the range -55 to 100eV, using all possible combinations of references (3 – 4 variables), all weights between 0 – 1 and forced to sum 1.

#### 3.4.2. μ-XRF and μ-XANES spectroscopy

μ-XRF mapping of Cu was performed at European Synchrotron Radiation Facility (ESRF) beamline ID21. Samples T1c60, T2c60, and S1c60 were scattered on the surface of sulphur free tape for analysis. The beam was focused with the use of a Fresnel zone plate to a size of 0.500 x 0.900 μm<sup>2</sup> (VxH). Incident energy was 9.1 keV and the fluorescence signal was detected by single element SDD 80 mm<sup>2</sup> active area, Bruker detector. Well time and distance of the detector were optimized for each XRF map keeping the dead time below 15 %. The XRF data was processed using PyMCA software (Solé *et al.*, 2007). The elemental distribution images were obtained by fitting the fluorescence emission peaks in the spectrum of each pixel and display the net intensity normalized by incoming beam for each element of interest. For μ-XANES data acquisition the energy was selected using a Si (111) double crystal monochromator and scanned from 8950 to 9150 eV. The zone plate was translated in the beam axis in order to maintain the beam focus.

μ-XRF mapping at 12.1 keV was performed at the Advanced Light Source (ALS) beamline 10.3. (Marcus *et al.*, 2004) in order to obtain co-localization with Cu and As. Sample T1c20 (<0.85 mm particle size) was embedded in epoxy resin, polished to 20 μm thickness and detached from the glass substrate for analysis. Maps were recorded using a 4 × 4 μm (V × H) beam at 12.1 keV with a 4 × 4 μm pixel size and a 30 ms dwell time. The fluorescence yield was measured with a seven-element germanium (Ge) solid-state fluorescence detector (Canberra 50 mm<sup>2</sup> per element) and normalized by I<sub>0</sub> and the dwell time.

## 4. Results and discussion

Total Cu content as determined by FAAS is shown in Table 1. For validation purposes selected samples were analyzed by XRF for total Cu content (XRF results in Table 3). Both methods agree in the values of Cu (p < 0.01) concentration and this supports the use of XRF as method for total quantification of Cu in mine tailings (for concentrations above tens of ppm). XRF is a non-destructive and least expensive technique compared to FAAS. Cu concentrations in mine tailings are in the range of 125 ± 21 and 1763 ± 10 mg·kg<sup>-1</sup> and in soils between 22 ± 5 and 88 ± 5 mg·kg<sup>-1</sup> (See Table 1). Soil reference samples collected from locations at 1.5 km distance from the mine tailings have Cu contents

Table 1. Total Cu content in  $\text{mg}\cdot\text{kg}^{-1}$  in mine tailings  $\pm$  S.D. in (T) soils (S) and reference (R) samples, collected at 1cm (s) and 30 cm (c) depth, grain sizes  $< 0.25$  mm (60),  $< 0.85$  mm (20).

Fraction Sample	Cu $\text{mg}\cdot\text{kg}^{-1}$		Fraction Sample	Cu $\text{mg}\cdot\text{kg}^{-1}$		Fraction Sample	Cu $\text{mg}\cdot\text{kg}^{-1}$	
	60	20		60	20		60	20
T1s	628 $\pm$ 21	452 $\pm$ 10	T7s	549 $\pm$ 46	564 $\pm$ 49	T13s	920 $\pm$ 84	547 $\pm$ 10
T1c	318 $\pm$ 28	217 $\pm$ 10	T7c	428 $\pm$ 41	373 $\pm$ 19	T13c	734 $\pm$ 57	561 $\pm$ 45
T2s	1763 $\pm$ 10	1411 $\pm$ 36	T8s	211 $\pm$ 13	125 $\pm$ 21	S1c	82 $\pm$ 5	33 $\pm$ 5
T2c	798 $\pm$ 27	574 $\pm$ 16	T8c	145 $\pm$ 17	125 $\pm$ 21	S2c	47 $\pm$ 7	41 $\pm$ 5
T3s	398 $\pm$ 33	377 $\pm$ 48	T9s	369 $\pm$ 29	308 $\pm$ 75	S3c	32 $\pm$ 5	22 $\pm$ 5
T3c	430 $\pm$ 7	400 $\pm$ 24	T9c	211 $\pm$ 18	219 $\pm$ 44	S4c	84 $\pm$ 5	88 $\pm$ 5
T4s	812 $\pm$ 12	967 $\pm$ 56	T10s	718 $\pm$ 31	675 $\pm$ 24	S5c	39 $\pm$ 5	29 $\pm$ 14
T4c	448 $\pm$ 23	407 $\pm$ 11	T10c	513 $\pm$ 5	675 $\pm$ 24	S1Rc	28 $\pm$ 5	22 $\pm$ 5
T5s	622 $\pm$ 81	821 $\pm$ 47	T11s	349 $\pm$ 16	316 $\pm$ 7	S2Rc	19 $\pm$ 5	11 $\pm$ 5
T5c	432 $\pm$ 15	434 $\pm$ 74	T11c	546 $\pm$ 8	465 $\pm$ 85	S3Rc	36 $\pm$ 5	27 $\pm$ 5
T6s	373 $\pm$ 83	970 $\pm$ 92	T12s	1363 $\pm$ 43	1311 $\pm$ 26			
T6c	871 $\pm$ 81	471 $\pm$ 47	T12c	451 $\pm$ 19	518 $\pm$ 38			

between  $11 \pm 5$  and  $36 \pm 5$   $\text{mg}\cdot\text{kg}^{-1}$ . The total Cu content in mine tailings is higher in the surface (top 1 cm) than in the composite 30 cm depth. In evaporation-controlled climate, it is possible that highly soluble Cu species could be mobilized by capillary force to the top mine tailings and once there, their mobility controlled by pH and sorption processes (Dold, 1999).

In order to determine Cu speciation and understand its influence to mobility in the environment, a combination of chemical extractions (SEP, phytoaccessibility and bioaccessibility), and XAS was used. Results from SEP showed that up to 80 % of the total Cu content in mine tailings is in the water soluble fraction (See Table 2). Cu repartition in tailings followed this trend: Water soluble > Residual > Organic bound > Exchangeable > Fe-Mn oxides bound > Carbonates bound. These results indicate the high mobility of Cu in the mine tailings. In soils, water soluble Cu represents the minor fraction. Cu repartition in soils was Residual > Organic bound > Fe-Mn oxides bound > Carbonates bound > Water soluble > Exchangeable. The results from SEP suggest Cu in the tailings is present as a highly mobile species and adsorption mechanisms to mineral and amorphous Fe oxides, Mn oxides, and clays do not primarily regulate its mobility. On the other hand, Soil Organic Matter is also a primary factor controlling Cu mobility (Yang *et al.*, 2014). However, Cu organic bound fraction in tailings is between 1 – 17 % and organic matter content is low, on average 1 % (data not shown). Cu association to Fe-oxide minerals can successfully control the mobility of Cu, because Cu binding at these minerals is resistant to sequential extractions up to residual fraction (Sracek *et al.*, 2010; Donner *et al.*, 2011). However, in this case, Cu bound to Fe-Mn-Oxides only represents between 1 to 7 % in mine tailings, despite of the high Fe content in the samples (between 108000 to 195000  $\text{mg}\cdot\text{kg}^{-1}$ ).

In order to understand how Cu in tailings and soils

may have an impact on the surrounding environment, the bioaccessible and phytoaccessible fractions were determined. According to the Mexican regulations, bioaccessibility is used to quantify the fraction of elements in soils that are soluble in a gastric media. For phytoaccessibility analysis we used an extraction with a solution of LWMOA, in order to simulate a chemical rhizosphere environment. Results showed that in most of the mine tailing samples between 50 and 99 % of total Cu content is available for plants and bioaccessible (see Table 3). In comparison, Cu in soils has limited availability for plants and no bioaccessible Cu was detected. These results agree with the SEP finding Cu mostly in the residual and organic bound fractions. The children's oral dose exposition was calculated using values from similar studies: 200  $\text{mg}\cdot\text{day}^{-1}$  soil ingest, 52 h of exposition and 52 kg weight for a child between 6 and 9 years (CEPIS, 1998). Doses involved in gastrointestinal disorders surpass an intake of 0.0731  $\text{mg}\cdot\text{kg}\cdot\text{day}^{-1}$  of Cu (ATSDR, 2004). All tested tailings surpassed this limit (with a range between 0.123 and 0.549  $\text{mg}\cdot\text{kg}\cdot\text{day}^{-1}$ ). Results suggest that there is high risk for environmental impact on plant community (phytoaccessible Cu) and to a lower level for human exposition (bioaccessible Cu).

Bulk and spatially resolved synchrotron techniques were used in order to investigate Cu speciation and associations with other elements in the mine tailings and soil. This approach is very powerful in samples where several chemical species are present (such as tailing and soil samples), the spatially resolved techniques provide confirmation on minor species that are not easy to identify in the bulk measurements. The references used for XANES LCF were  $\text{Cu}^{+2}\text{SO}_4$  as model for  $\text{Cu}^{+2}$  highly soluble species and associated to inorganic and organic matter,  $\text{Cu}^{+1}\text{O}_2$  to account for  $\text{Cu}^{+1}$  species with oxygen ligands,  $\text{Cu}^{+1}\text{FeS}_2$  to account for  $\text{Cu}^{+1}$  species with S ligands (and also since this is main mineral phase in ore), and finally  $\text{Cu}^{+2}_3\text{AsO}_4(\text{OH})_3$

Table 2. Cu Sequential extraction fractions in mg·kg<sup>-1</sup> in mine tailings ± S.D. and % from total content of mine tailings (T), soils (S) and reference (R) samples, collected at 1 cm (s) and 30 cm (c) depth, grain sizes < 0.25 mm (60) and < 0.85 mm (20). nd; no detected.

Step Fraction Sample	Water soluble		Exchangeable		Bound to carbonates		Bound to Fe-Mn-Oxides		Organic Bound		Residual	
	60	20	60	20	60	20	60	20	60	20	60	20
T1s	366±18 (80%)	413±11 (71%)	21±5 (5%)	19±5 (3%)	nd	nd	9±5 (2%)	8±5 (1%)	18±5 (4%)	17±5 (3%)	36±9 (8%)	124±8 (21%)
T1c	113±5 (26%)	168±49 (46%)	13±5 (3%)	11±5 (6%)	nd	nd	8±5 (2%)	7±5 (2%)	13±5 (3%)	15±5 (4%)	283±5 (65%)	159±8 (44%)
T2s	841±16 (81%)	1184±39 (75%)	54±5 (5%)	33±5 (3%)	6±5 (1%)	6±5 (<1%)	6±5 (1%)	7±5 (<1%)	18±5 (2%)	22±5 (1%)	111±7 (11%)	310±29 (20%)
T2c	519±23 (76%)	444±66 (73%)	45±5 (5%)	48±5 (8%)	nd	nd	7±5 (1%)	7±5 (1%)	19±5 (3%)	22±5 (4%)	97±5 (14%)	79±9 (13%)
T10s	379±11 (54%)	406±70 (63%)	34±5 (5%)	7±5 (5%)	nd	nd	39±5 (6%)	26±6 (4%)	91±5 (13%)	97±5 (15%)	125±5 (18%)	47±5 (7%)
T10c	351±20 (67%)	27±5 (6%)	7±5 (1%)	6±5 (1%)	nd	nd	37±5 (7%)	36±5 (8%)	85±5 (16%)	82±5 (17%)	33±5 (6%)	305±6 (65%)
T12s	1129±65 (83%)	1360±112 (87%)	52±5 (4%)	53±5 (3%)	14±5 (1%)	13±5 (1%)	16±5 (6%)	15±6 (1%)	42±23 (3%)	52±5 (3%)	36±5 (3%)	67±24 (4%)
T12c	333±21 (72%)	352±54 (68%)	30±5 (7%)	26±5 (5%)	9±5 (2%)	9±5 (2%)	15±5 (3%)	8±5 (3%)	39±5 (9%)	37±5 (7%)	33±5 (7%)	78±10 (15%)
S1c	22±5 (21%)	17±5 (20%)	nd	nd	nd	nd	6±5 (8%)	nd	31±5 (31%)	14±5 (17%)	34±5 (33%)	40±5 (48%)
S2c	nd	nd	nd	nd	nd	nd	nd	nd	18±5 (41%)	11±5 (26%)	15±5 (35%)	26±5 (61%)
S1Rc	nd	nd	nd	nd	nd	nd	nd	nd	8±5 (26%)	7±5 (34%)	13±5 (41%)	6±5 (25%)

Table 3. Summary table of chemical extraction Cu content in mg·kg<sup>-1</sup> ± S.D. and synchrotron analysis from selected mine tailings (T), soils (S) and reference (R) samples, collected at 1cm (s) and 30 cm (c) depth, grain sizes < 0.25 mm (60) and < 0.85 mm (20). nd; no detected, empty cells; no data available/no analysed.

Technique Fraction Sample	XRF mg·kg <sup>-1</sup>		Phytoaccessibiity mg·kg <sup>-1</sup>		Bioaccessibility mg·kg <sup>-1</sup>		XANES		μ-XANES		μ-XRF		SEP	
	60	20	60	20	60	20	60	20	60	20	60	20	60	20
T1s	520±43	1400±92	611±10	408±8	593±5		✓	✓					✓	✓
T1c	249±30	370±37	305±8	142±8	296±5		✓		✓		✓	✓	✓	✓
T2s	1310±84	547±48	1700±14	1398±18	599±5		✓						✓	✓
T2c	734±57	561±45	721±8	514±47	601±5		✓		✓		✓		✓	✓
T10s			414±5	350±17	480±8								✓	✓
T10c			15±5	18±5	71±7								✓	✓
T12s			1204±47	1255±5	1320±29								✓	✓
T12c			299±39	373±10	343±23								✓	✓
S1c	102±16	105±16	nd	nd	12±5		✓		✓		✓		✓	✓
S2c			12±7	6±5	nd								✓	✓
S1Rc			nd	nd	nd								✓	✓

(clinoclase) as suggested by the correlation of As and Cu in μXRF map from sample T1c20 (see Figure 2(A) R1, R2). The As-Cu correlation can be observed in the tricolor image Figure 2A in pixels with a yellow to orange color obtained by the overlay of Cu (green) and As (red). The total content of As in the mine tailings reaches up to 12000 mg·kg<sup>-1</sup> in the tailings and 300 mg·kg<sup>-1</sup> in soils, geochemical studies of As are also being conducted to investigate its mobility. Figure 1 shows the XANES LCF results obtained with the use of the selected references for one mine tailing and one soil, samples T1c60 and S1c60. Results from all samples analyzed by bulk-XANES are shown in Table 4. Results showed that Cu in mine tailing samples is mainly present as Cu<sup>2+</sup> species (which as suggested by SEP is a highly mobile species) and clinoclase (Cu<sub>3</sub>(AsO<sub>4</sub>)(OH)<sub>3</sub>). XRF maps suggest Cu in the tailing soluble fraction could not only be present as CuSO<sub>4</sub>, since S is mainly co-localized with Ca (Pearson correlation 0.867). This Cu<sup>2+</sup> highly soluble species in tailings is potentially a mixture of CuSO<sub>4</sub> of varied crystallinities and hydration levels and forming soluble Cu complexes with organic acids derived from microorganism exudates (Ebena et al., 2007; Xie et al.,

2010). The percentages of clinoclase obtained in the fit might not be accurate since clinoclase presents a XANES spectrum similar to other Cu<sup>2+</sup> species (bound to organic matter and adsorbed to oxides), hence it is difficult to accurately distinguish Cu<sup>2+</sup> species based on their XANES signal. Another Cu arsenate reference (olivenite) was tested but fittings were of better quality with clinoclase. The presence of clinoclase requires confirmation and for that spatially resolved synchrotron micro X-ray Diffraction experiments will be performed on these samples in a future experiment. Cu<sup>1+</sup> species bound to oxygen ligands (as in CuO<sub>2</sub>) were rarely detected in the mine tailing samples (5 % in T1s60), which confirms Cu<sup>1+</sup> is not an abundant species. The presence of another low abundance species (Cu<sup>1+</sup>FeS<sub>2</sub>, chalcopyrite) in the tailing samples was confirmed with the use of μ-XRF mapping and μ-XANES (see Figure 2 (B, D)). Chalcopyrite is commonly distributed in the earth crust, but due to its low solubility it does not represents a risk for Cu mobility in natural conditions (Dold, 1999). The soil XANES LCF results showed a decreased contribution of Cu<sup>2+</sup> mobile species and higher contribution from the reference Cu<sup>2+</sup> arsenate (clinoclase). This Cu<sup>2+</sup> species has a

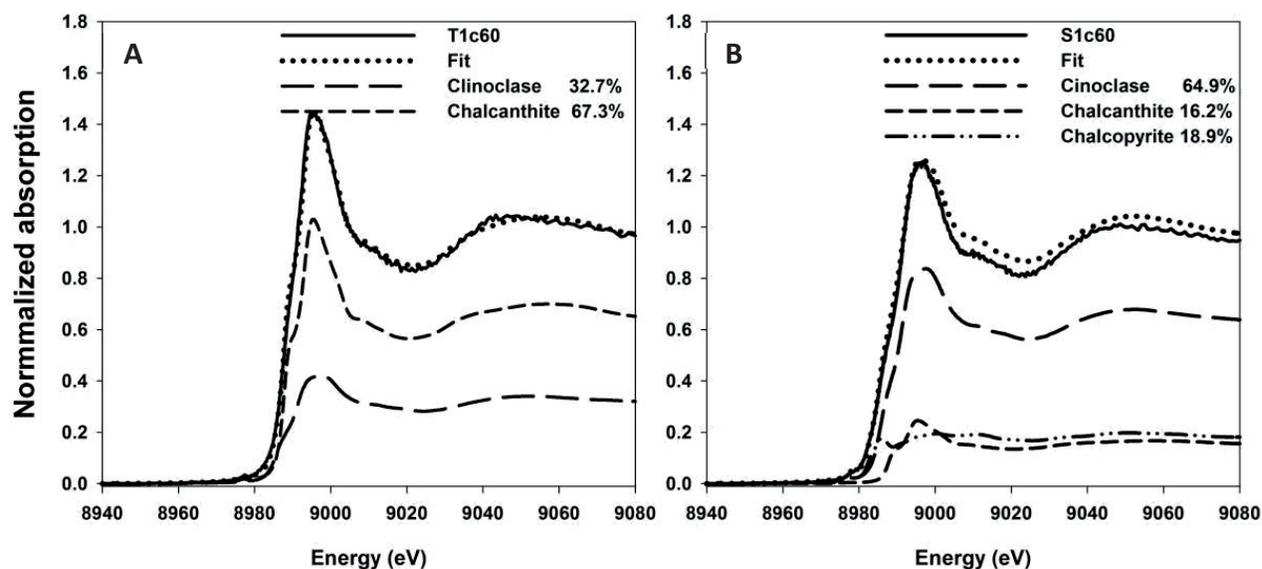


Figure 1. Linear combination analysis of representative tailing (A) and soil (B) samples, using clinoclase ( $\text{Cu}_3\text{AsO}_4(\text{OH})_3$ ), chalcantinite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and chalcopyrite ( $\text{CuFeS}_2$ ) as reference spectra.

Table 4. Weight of components from Bulk XANES Linear combination analysis in some tested mine tailings (T) and soils (S) samples, collected at 1 cm (s) and 30 cm (c) depth, grain size < 0.25 mm (60).

Sample	Components			Results	
	Clinoclase $\text{Cu}_3\text{AsO}_4(\text{OH})_3$	Chalcantinite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Chalcopyrite $\text{CuFeS}_2$	$\text{Cu}_2\text{O}$	R-factor
T1s60	0.342	0.606	0	0.052	0.0018
T1c60	0.327	0.673	0	0	0.0015
T2s60	0.404	0.596	0	0	0.0013
T2c60	0.225	0.775	0	0	0.002
S1c60	0.649	0.162	0.189	0	0.008

low solubility constant ( $7.6 \times 10^{-36}$ ) (Magalhaes and Pedrosa de Jesus, 1988) and it could explain the low water soluble and exchangeable values of Cu obtained by SEP. Clinoclase occurs in arsenate and sulphate rich environments at oxidized conditions, the most common secondary mineral in this environment is olivenite at slightly acidic pH (4–6) but around neutral pH, clinoclase is predominant (Williams, 1990). In soil samples pH range is 7.3–8.2. In soils the mobility of Cu is possibly controlled by the formation of secondary minerals (Clinoclase) or adsorption to organic matter. In addition to this,  $\mu$ -XANES spectra from the soil composite sample (S1c60) presents a near-edge feature characteristic of  $\text{Cu}^{+1}$  (as in  $\text{CuO}_2$ ) which confirms the presence of  $\text{Cu}^{+1}$  species bound to oxygen ligands and co-localized with Fe (see Figure 2 (C, D)). This result suggests the formation of  $\text{Cu}^{+1}\text{FeO}_2$  in the soil sample (Sukeshini *et al.*, 2000). The bulk XANES analysis of the soil sample also suggests  $\text{Cu}^{+1}\text{FeS}_2$  (chalcopyrite) is present in the soil and the origin of this species might be linked to mechanical transport of particles (water and wind erosion).

## 5. Conclusions

In summary, Cu is present as a highly  $\text{Cu}^{+2}$  mobile species in the mine tailings that could be moving towards surrounding soil in water solution and via wind and water erosion. In soils Cu is predominantly  $\text{Cu}^{+2}$  but as confirmed by SEP in the form of a less mobile Cu species. The formation of a Cu-arsenate species is likely due to the high content of As and co-localization observed from  $\mu$ XRF maps. However, adsorption to amorphous and crystalline Fe and Mn oxides and associations to organic matter are likely to occur in the soil. The presence of  $\text{Cu}^{+1}$  species as oxides and sulphides was also confirmed by  $\mu$ XRF/XANES results but represent only a minor fraction in both tailing and soil. Since, water soluble and exchangeable Cu in soil is low; the highly mobile Cu from the tailings could be reaching further from our tested sampling site and even filtrating further than the 30 cm sampled depth in the soil. The results of this research report also on the high potential impact to plants in this site since phytoaccessible Cu is higher than 50 %.

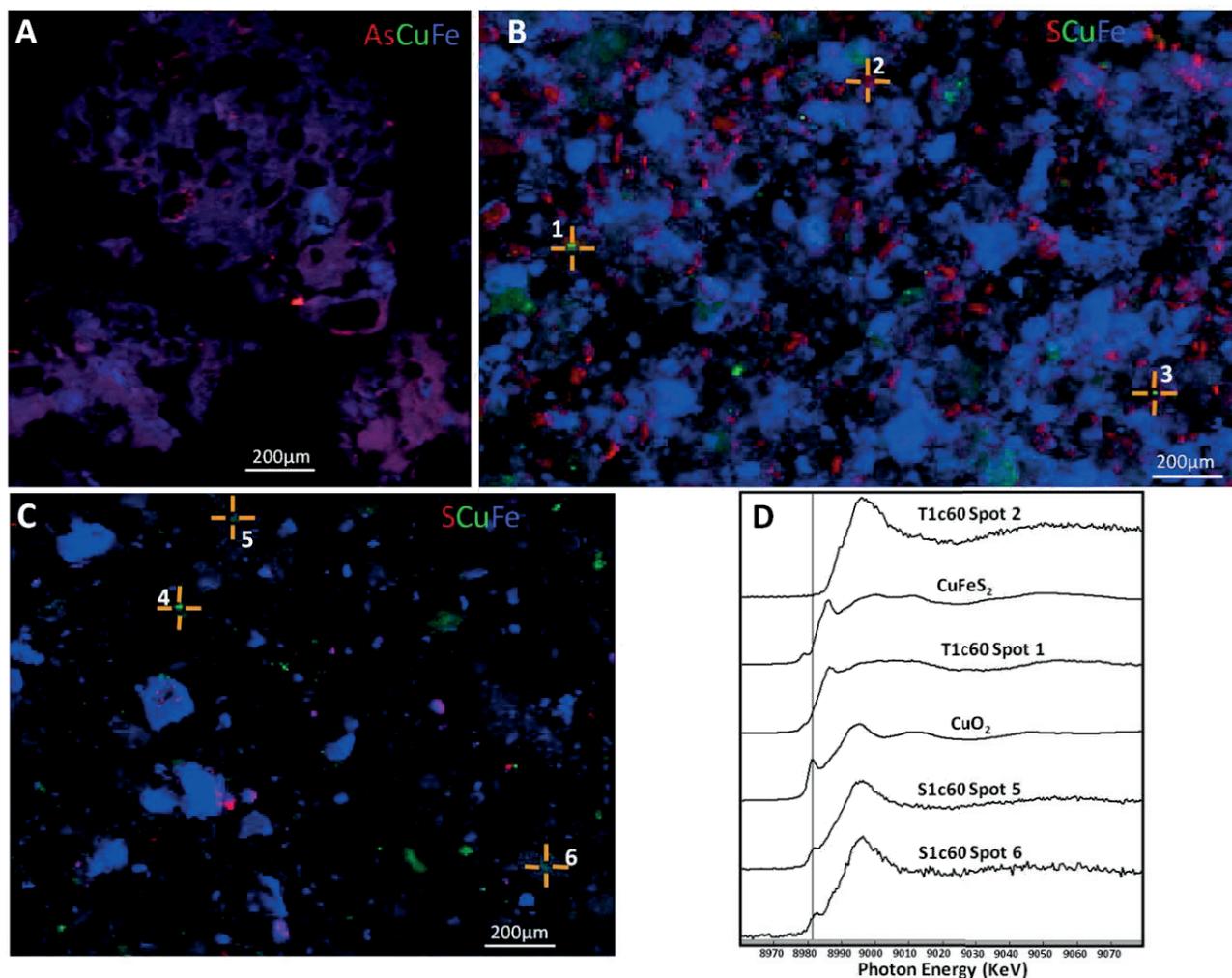


Figure 2.  $\mu$ -XRF maps and  $\mu$ -XANES spectra. A)  $\mu$ -XRF map at 12.1 keV incident energy from sample T1c20 (embedded thin section). B)  $\mu$ -XRF map at 9.2 keV incident energy from sample T1c60. C)  $\mu$ -XRF map at 9.2 keV incident energy from sample S1c60. D)  $\mu$ -XANES spectra from label spots indicated in B and C and reference compounds  $\text{CuFeS}_2$  and  $\text{CuO}_2$ .

Further experiments should be performed in order to quantify Cu concentration in plants from the region and determine the impact to plant community. For human health, this site is also potential threat due to the elevated Cu content which surpasses in some cases the dose involved in gastrointestinal diseases and liver damage. More sampling points should be analysed using the present approach (SEP-XAS- $\mu$ -XRF/XANES) in order to better understand the mobility of Cu in the site and the impact on environmental and human health. However, one disadvantage of synchrotron based techniques is the lack of availability of the instruments and the short time of experimentation which is allocated for each user group. The present work has illustrated the importance of a multianalytical, multiscale approach for the understanding of geochemical processes that are involved in the mobilization and speciation of potentially toxic elements (such as Cu).

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