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

René Loredo Portales, Gustavo Cruz Jiménez, Hiram Castillo Michel, Diana Olivia Rocha Amador, Katarina Vogel Mikus, Peter Kump, Guadalupe de la Rosa

1 Department of Pharmacy, University of Guanajuato, Noria alta, 36050 Guanajuato, Guanajuato, Mexico.
2 ID 21, European Synchrotron Radiation Facility, Avenue des Martyrs 71, 3800 Grenoble, France.
3 Department of Biology, University of Ljubljana, Večna pot 111, 1000 Ljubljana, Slovenia.
4 Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.
5 Biomedical and Electrical Engineering, University of Guanajuato, Lomas del Bosque 103, 37150 Leon, Guanajuato, Mexico.

Abstract

Potentially toxic elements are usually present in mine tailings in concentrations that may threat 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 ± 21 and 1763 ± 10 mg·kg⁻¹ and 22 ± 2 and 88 ± 5 mg·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 Cu²⁺, forming highly mobile species, and in minor proportion as Cu¹⁺ 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 Exacciones Secuenciales, Espectroscopia 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 ± 21 y 1763 ± 10 mg·kg⁻¹ y 22 ± 2 a 88 ± 5 mg·kg⁻¹. La distribución de Cu en los jales determinada por las Exacciones 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.
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 mg·kg·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 ≥ 0.06 mg L$^{-1}$ in soil solution. The critical range for toxicity in leaves are between 20 – 30 mg·kg$^{-1}$ for crop species and around 18 mg·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 mg·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 mg·kg$^{-1}$ in soils near the Chilean Cu mine tailings of “La Cocinera”. Cu content in soils exceeding 200 mg·kg$^{-1}$ are considered as anomalous (Bowie and Thorton, 1985). Regulations for Cu in soils are between 50 (Holland) to 1000 mg·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 (µ-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 (µ-XANES) and µXRF 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 µ-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 phytotoxicity 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 km NW of Xichú town, in Guanajuato, Mexico, 393071 m N and 2359296 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 masl. The weather is semi arid with summer rains, and temperatures range between 18 to 22 °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, µ-XRF and µ-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 HNO₃ (Reagent grade; Fermont) were added. Mixtures were boiled for about 1 h with a reflux condenser. Later, 3 mL of H₂O₂ (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 µm 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. ¹⁰⁹Cd (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-μm-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-Grieven, 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 ± 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 ± 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 µm 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⁻¹, 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 Cieśliński et al. (1998): acetic acid (C₂H₄O₂; 2898 mM), succinic (C₄H₆O₄; 194 mM), oxalic (H₂C₂O₄; 43 mM), malic (C₄H₆O₅; 39.8 mM), tartaric (C₄H₄O₆; 26.3 mM), fumaric (C₂H₄O₄; 12 mM) and citric acid (C₆H₈O₇; 6 mM). Extraction was performed using 1 g of sample and the LWMOA solution in a 1:15 proportion (pH 4.5 ± 0.1). Solutions were shaken for 5 h, centrifuged at 3000 x g, filtered with a 2.5 µ 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 MgCl₂ (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 solid residue from the previous step, and stirred for 5 h at room temperature; 5) Organic bound, 3 mL of 0.02 M HNO₃ residue from the previous step, during 6 h at 96 °C with occasional stirring; 6) Residual was extracted with 5 mL of 30 % H₂O₂ (pH 2 with HNO₃), heated during 2 h at 85 °C with occasional stirring, after that another 3 mL of H₂O₂ (pH 2 with HNO₃) was added, heated during 3 h at 85 °C with occasional stirring; 7) Residual was extracted with acid extraction with HNO₃ and H₂O₂. 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 (Whatman ©), 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 Elekta 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 (Cu₃AsO₄(OH)₃), copper(II) sulfate/chalcanthite (CuSO₄·5H₂O), copper(II) oxide (CuO), copper(I) oxide (Cu₂O), olivenite (Cu₃AsO₄OH), and copper acetate (Cu(CH₃COO)₂). 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 purchased as reagent grade chemicals from sigma Aldrich.

XANES data was calibrated with the use of a Silicon Drift Detector (SDD; KETEK GmbH AXAS-M with an assembled 80 mm² 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 Cu₂O-foil and scanned 120 eV below the edge (5 eV 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 100 eV, 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 μm² (VxH). Incident energy was 9.1 keV and the fluorescence signal was detected by single element SDD 80 mm² 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 x 4 μm (V x H) beam at 12.1 keV with a 4 x 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 mm² per element) and normalized by I₀, 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⁻¹ and in soils between 22 ± 5 and 88 ± 5 mg kg⁻¹ (See Table 1). Soil reference samples collected from locations at 1.5 km distance from the mine tailings have Cu contents
Copper speciation and mobilization in mine wastes in central Mexico

The total Cu content between 11 ± 5 and 36 ± 5 mg∙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 mg∙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 mg∙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 mg∙kg∙day⁻¹ of Cu (ATSDR, 2004). All tested tailings surpassed this limit (with a range between 0.123 and 0.549 mg Cu∙kg∙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 Cu²⁺SO₄ as model for Cu²⁺ highly soluble species and associated to inorganic and organic matter, Cu¹⁺O₂ to account for Cu¹⁺ species with oxygen ligands, Cu¹⁺FeS₂ to account for Cu¹⁺ species with S ligands (and also since this is main mineral phase in ore), and finally Cu²⁺,AsO₄(OH)₃

### Table 1. Total Cu content in mg∙kg⁻¹ in mine tailings ± S.D. in (T) soils (S) and reference (R) samples, collected at 1 cm (s) and 30 cm (c) depth, grain sizes < 0.25 mm (60), < 0.85 mm (20).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Cu mg∙kg⁻¹</th>
<th>Fraction</th>
<th>Cu mg∙kg⁻¹</th>
<th>Fraction</th>
<th>Cu mg∙kg⁻¹</th>
</tr>
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<tbody>
<tr>
<td>Sample</td>
<td>60  20</td>
<td>Sample</td>
<td>60  20</td>
<td>Sample</td>
<td>60  20</td>
</tr>
<tr>
<td>T1s</td>
<td>628 ± 21</td>
<td>T7s</td>
<td>549 ± 46</td>
<td>T13s</td>
<td>920 ± 84</td>
</tr>
<tr>
<td>T1c</td>
<td>318 ± 28</td>
<td>T7c</td>
<td>428 ± 41</td>
<td>T13c</td>
<td>734 ± 57</td>
</tr>
<tr>
<td>T2s</td>
<td>1763 ± 10</td>
<td>T8s</td>
<td>211 ± 13</td>
<td>S1c</td>
<td>82 ± 5</td>
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<td>T2c</td>
<td>798 ± 27</td>
<td>T8c</td>
<td>145 ± 17</td>
<td>S2c</td>
<td>47 ± 7</td>
</tr>
<tr>
<td>T3s</td>
<td>398 ± 33</td>
<td>T9s</td>
<td>369 ± 29</td>
<td>S3c</td>
<td>32 ± 5</td>
</tr>
<tr>
<td>T3c</td>
<td>430 ± 7</td>
<td>T9c</td>
<td>211 ± 18</td>
<td>S4c</td>
<td>84 ± 5</td>
</tr>
<tr>
<td>T4s</td>
<td>812 ± 12</td>
<td>T10s</td>
<td>718 ± 31</td>
<td>S5c</td>
<td>39 ± 5</td>
</tr>
<tr>
<td>T4c</td>
<td>448 ± 23</td>
<td>T10c</td>
<td>513 ± 5</td>
<td>S1Rc</td>
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<tr>
<td>T5s</td>
<td>622 ± 81</td>
<td>T11s</td>
<td>349 ± 16</td>
<td>S2Rc</td>
<td>19 ± 5</td>
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<tr>
<td>T5c</td>
<td>432 ± 15</td>
<td>T11c</td>
<td>546 ± 8</td>
<td>S3Rc</td>
<td>36 ± 5</td>
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<td>T6s</td>
<td>373 ± 83</td>
<td>T12s</td>
<td>1363 ± 43</td>
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</tr>
<tr>
<td>T6c</td>
<td>871 ± 81</td>
<td>T12c</td>
<td>451 ± 19</td>
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Between 11 ± 5 and 36 ± 5 mg∙kg⁻¹.
Loredo Portales et al.

452

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\(^{-1}\) in the tailings and 300 mg·kg\(^{-1}\) 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\(^{2+}\) species (which as suggested by SEP is a highly mobile species) and clinoclase (Cu\(_3\)(AsO\(_4\))(OH)\(_3\)). XRF maps suggest Cu in the tailing soluble fraction could not only be present as CuSO\(_4\), since S is mainly co-localized with Ca (Pearson correlation 0.867). This Cu\(^{2+}\) highly soluble species in tailings is potentially a mixture of CuSO\(_4\) 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\(^{2+}\) species (bound to organic matter and adsorbed to oxides), hence it is difficult to accurately distinguish Cu\(^{2+}\) 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\(^{1+}\) species bound to oxygen ligands (as in CuO\(_2\)) were rarely detected in the mine tailing samples (5 % in T1s60), which confirms Cu\(^{1+}\) is not an abundant species. The presence of another low abundance species (Cu\(^{1+}\)FeS\(_2\), 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\(^{2+}\) mobile species and higher contribution from the reference Cu\(^{2+}\) arsenate (clinoclase). This Cu\(^{2+}\) species has a
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 %.  

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).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clinoclase (\text{Cu}_3\text{AsO}_4(\text{OH})_3)</th>
<th>Chalcanthite (\text{CuSO}_4\cdot5\text{H}_2\text{O})</th>
<th>Chalcopyrite (\text{CuFeS}_2)</th>
<th>(\text{Cu}_2\text{O})</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1s60</td>
<td>0.342</td>
<td>0.606</td>
<td>0</td>
<td>0.052</td>
<td>0.0018</td>
</tr>
<tr>
<td>T1c60</td>
<td>0.327</td>
<td>0.673</td>
<td>0</td>
<td>0</td>
<td>0.0015</td>
</tr>
<tr>
<td>T2s60</td>
<td>0.404</td>
<td>0.596</td>
<td>0</td>
<td>0</td>
<td>0.0013</td>
</tr>
<tr>
<td>T2c60</td>
<td>0.225</td>
<td>0.775</td>
<td>0</td>
<td>0</td>
<td>0.002</td>
</tr>
<tr>
<td>S1c60</td>
<td>0.649</td>
<td>0.162</td>
<td>0.189</td>
<td>0</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Figure 1. Linear combination analysis of representative tailing (A) and soil (B) samples, using clinoclase \((\text{Cu}_3\text{AsO}_4(\text{OH})_3)\), chalcanthite \((\text{CuSO}_4\cdot5\text{H}_2\text{O})\) and chalcopyrite \((\text{CuFeS}_2)\) as reference spectra.
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-µ-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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