

# Evaluation of metal mobility from copper mine tailings in northern Chile

Elizabeth J. Lam<sup>1</sup> · M. E. Gálvez<sup>1</sup> · M. Cánovas<sup>2</sup> · I. L. Montofré<sup>1</sup> · D. Rivero<sup>1</sup> · A. Faz<sup>3</sup>

Received: 19 August 2015 / Accepted: 1 March 2016 / Published online: 9 March 2016  
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**Abstract** This work shows the results obtained on a copper mine tailing in the Antofagasta Region, Chile. The tailing was classified as saline-sodic with high concentrations of metals, especially Cu and Fe, with pH 8.4. Our objectives were to (1) compare the physicochemical properties of the tailing with surrounding soils of the mine under study, and (2) evaluate the effect of two amendments (CaCO<sub>3</sub> and compost) and their mixtures on Cu<sup>2+</sup>, Mn, Fe, Zn, Mg<sup>2+</sup>, and K<sup>+</sup> and Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> leaching. The data obtained were submitted to variance and covariance analysis. The results from the comparison between both substrates showed that in general, the tailing presented greater content of metals. Regarding tailing leaching, pH, electrical conductivity (EC), and concentration of the elements of interest were measured. The statistical analysis showed that Cu<sup>2+</sup> leaching and immobilization of Fe occurred to the greatest extent with compost. The EC decreased throughout the experiment with irrigation and increased upon treatment with compost. The major interactions found among the chemical parameters were (1) tailings without treatment, Cu<sup>2+</sup>/Fe and NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup>; (2) tailings treated with CaCO<sub>3</sub>, Cu<sup>2+</sup>/K<sup>+</sup>; (3) tailings treated with compost, NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> and EC/Cu<sup>2+</sup>; and (4) tailings treated with

both amendments, EC/Fe and Cu<sup>2+</sup>/Fe. The ANOVA showed that the number of irrigations and the amendments statistically significantly affected the copper mobility and the organic amendment significantly influenced the iron mobility.

**Keywords** Copper mine tailings · Leaching columns · Mobility · Heavy metals · Amendments

## Introduction

Mining is the principal economic activity in Chile, and the Atacama Desert in northern Chile is one of the most important copper mining regions in the world. Because of the large mineral deposits, located mainly in the Antofagasta Region, large amounts of investments are planned in the coming years. According to the National Mining Society of Chile, mining investment in the Antofagasta Region to 2016 is projected at US\$30 billion. Mining is also responsible for significant environmental damage, such as air pollution caused by particulate matter, toxic air emissions from foundries, and pollution and depletion of surface and groundwater resources (Kitula 2006; Coelho et al. 2007).

When mining operations come to an end, large volumes of solid wastes are stored in the mine. These wastes, known as mine tailings, are composed mainly of fine-grained mineral particles with high concentrations of heavy metals (As, Cd, Cu, Fe, Hg, Pb, Zn, etc.) and pH values in the strongly acidic to alkaline range (Krzaklewski and Pietrzykowski 2002; Mendez and Maier 2008). Historically, tailings in Chile were abandoned without proper management, due to a lack of adequate legislation. Current Chilean mining legislation requires that tailings be physically and chemically stabilized. Mining companies are now required to have a closure plan to ensure

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Responsible editor: Philippe Garrigues

✉ Elizabeth J. Lam  
elam@ucn.cl

<sup>1</sup> Chemical Engineering Department, Universidad Católica del Norte, Antofagasta, Chile

<sup>2</sup> Metallurgical and Mining Engineering Department, Universidad Católica del Norte, Avda. Angamos 0610, Antofagasta, Chile

<sup>3</sup> Agrarian Science and Technology Department, Universidad Politécnica de Cartagena, Paseo Alfonso XIII 48, 30203 Cartagena, Spain

the stability of tailing landfills to safeguard the surrounding environment and the health of the local population.

This work was carried out in a copper mine tailing in the Antofagasta Region, one of the driest zones in the world. The tailing was classified as saline-sodic, with low Ca and high Na and  $\text{SO}_4^{2-}$  contents; high concentrations of metals such as Cu, Fe, and Al; and pH 8.4. The tailing under study presents high concentrations of  $\text{SO}_4^{2-}$  and sulfides, which can generate sulfuric acid by oxidation and irrigation. The effects on the tailings of the two chosen amendments,  $\text{CaCO}_3$  and commercial compost, were evaluated using the undisturbed soil columns.

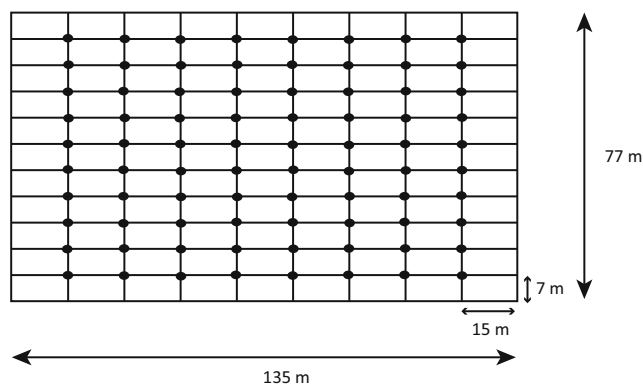
Two endemic species, *Adesmia atacamensis* and *Cistanthe salsoides*, were found in the area surrounding the tailing. The results of this work may help to identify the effect of amendments with a potential for phytoremediation in subsequent studies. The substrate-amendment-chemical species interaction was evaluated to determine the mobility and bioavailability of chemical species. In this context, the main objectives of this work were to (1) evaluate the effect of two amendments ( $\text{CaCO}_3$  and compost) and their mixtures on the mobility and bioavailability of specific elements, using column leaching experiments and (2) compare the physical and chemical properties of the surrounding soil and the tailing under study as a preliminary evaluation for potential phytoremediation using endemic species.

## Material and methods

### Copper mine tailing samples

This study was conducted in the Antofagasta Region of Chile, in the Atacama Desert. This region is characterized by high levels of solar radiation, high saline concentrations in the soil, extremely high daytime temperatures, and a wide day-night temperature range. Some areas of the Atacama Desert have zero recorded rainfall in 400 years. In general, rainfall occurs every 100 years. All of these conditions produce scarce vegetation. Samples were collected from a copper mine tailing site located at latitude  $24^\circ 9' 58.33''$  S and longitude  $69^\circ 2' 33.36''$  W at an altitude of 3200 m.a.s.l. The terraces where the tailings are located have high concentrations of heavy metals such as Cu, Cd, Fe, Zn, Mn, and Pb, because the tailings are generated in the process of sulfide concentration. The approximate total area of the terrace is  $10,000 \text{ m}^2$  ( $135 \times 77 \text{ m}^2$ ). This site was used as a tailing dump from 1995 to 2006.

To collect the samples, the terrace was divided into a grid of  $15 \text{ m} \times 7 \text{ m}$ , covering an internal area of  $6615 \text{ m}^2$ , to create 80 equidistant sampling points, as shown in Fig. 1. Due to the rough terrain and to facilitate sample collection, the profiles corresponding to external points of the terrace were not considered. For the 80 internal points, intensity of magnetic susceptibility was measured at the surface (depth 0–10 cm) using



**Fig. 1** Graphical representation of the 80 equidistant sampling points

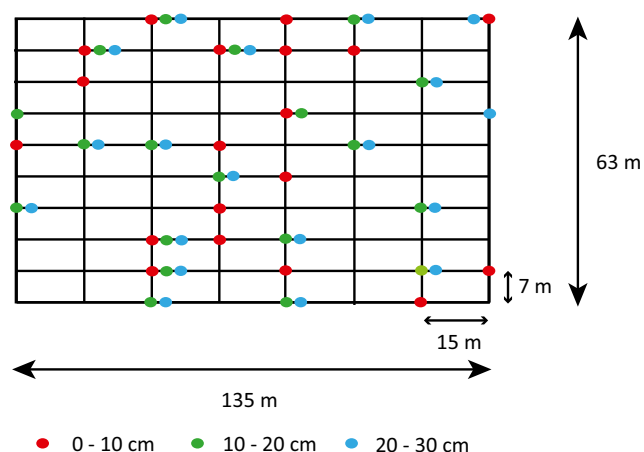
a magnetometer AGM2900. This property was used to estimate the points with larger metal concentrations (Durza et al. 1993). According to this criterion, 33 sample points were selected.

For the selected points, four undisturbed cylindrical samples of 0.05-m diameter and 0.1-m depth were collected at three depths (0–10, 10–20, and 20–30 cm), obtaining 1 kg of soil at each depth level (see Fig. 1). As preliminary fieldwork, the soil profile characteristics were determined using the Munsell Soil Color Chart (Color, Munsell 2009). The soil color profile was measured for each depth of the sample point. Those sample points in which the contiguous depths presented the same color were considered homogeneous; therefore, only one of them was selected for the physicochemical analysis. With the application of this methodology, a total of 57 samples were analyzed (see Fig. 2). On the other hand, ten samples at a depth of 20 cm were collected from the surrounding soil. The measured parameters included Fe, Mn, Cu, Zn, Pb, Cd, Cr, Al, Mo, As, B,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , pH, water saturation, and electrical conductivity (EC) of the soil.

### Sample analysis

Substrate samples of about 1 kg were collected, properly labeled and packed in polyethylene bags. They were oven-dried at  $40^\circ \text{C}$  until reaching a constant weight (Fellet et al. 2007; Marchiol et al. 2007). Rocks, stones, and any other extraneous materials were removed, and the remaining particles were reduced in size with a mortar and pestle. Particles were then screened with a 2-mm sieve (US N° 10 mesh), which is the standard particle size for most soil testing methods (Fellet et al. 2007; Clemente et al. 2008).

Bioavailable Fe, Mn, Zn, Cr, Cu, Cd, and Pb contents were measured by an atomic absorption spectrophotometer after extraction using a diethylenetriaminepentaacetic acid (DTPA) solution (Lindsay and Norvell 1978). These metals were extracted by shaking 0.01 kg of oven-dried soil for 2 h in 20 mL of 0.005 M DTPA. The filtrate was analyzed for Fe, Mn, Zn, Cr, Cu, Cd, and Pb by AAS. The analysis for As was



**Fig. 2** Location of soil sample points and their depth

carried out separately by hydride generation atomic absorption spectrometry (HG-AAS). Hydride was generated using a Perkin-Elmer 100 FIAS system (Hartley et al. 2004). All solutions were filtered with Whatman GF/C fiberglass filter paper.

Boron was extracted (Bingham 1982; Watson 1998) by boiling 0.025 kg of oven-dried soil under reflux with 50 mL of 0.01 M CaCl<sub>2</sub> for 5 min in fiber digestion equipment. The samples were cooled and then filtered through a 0.45-μm PTFE, and the filtrate was acidified and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Fassel and Kniseley 1974; Dahlquist and Knoll 1978). Aluminum was extracted from the tailing using potassium chloride (1 M, 1:10 w/v tailing: extractant ratio, 30-min shaking). Aluminum in the filtrate was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Blakemore et al. 1972; Westerman 1990). Molybdenum was analyzed by inductively coupled plasma-atomic emission spectrometry after partial digestion with HCl-H<sub>2</sub>O<sub>2</sub> leach and DIBK extract (Briggs 1996).

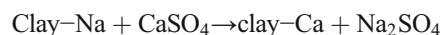
Chloride and SO<sub>4</sub><sup>2-</sup> anions (Nieto and Frankenberger 1985a, b) and K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> cations (Nieto and Frankenberger 1985b; Basta and Tabatabai 1985) were determined by ionic chromatography (Metrohm 861-CompactIC). The pH was measured potentiometrically from the saturated paste extract (SPE) using a pH meter. This method involves saturating the material with water and subsequently extracting the liquid phase under partial vacuum. Electrical conductivity was measured in the saturated paste extract with a conductivity cell (Rhoades et al. 1989). Water saturation percentage was calculated as the sum of the water added and that initially present in the field, expressed on an oven-dry basis.

**Amendments and doses**

The tailing under study had low Ca<sup>2+</sup> concentration (≈300 mg kg<sup>-1</sup>), with high levels of metal sulfides, such as

pyrite and sulfide wastes, and H<sub>2</sub>SO<sub>4</sub> is produced by oxidation and irrigation. It is expected that H<sub>2</sub>SO<sub>4</sub> reacts with CaCO<sub>3</sub> and produces gypsum, which has the same effect as the direct application of gypsum, but with the potential advantage of inhibiting the toxic effects of H<sub>2</sub>SO<sub>4</sub> on plant development. Application of gypsum is a common recommendation as a source of calcium to replace exchangeable sodium and to reduce alkalinity and improve physical and chemical properties of the soil (Choudhary et al. 2004).

Based on the above discussions, CaCO<sub>3</sub> was chosen as the inorganic amendment. CaCO<sub>3</sub> was obtained from eggshells, which are a rich source of mineral salts, mainly calcium carbonate that makes up about 94 % of the shell, with small amounts of magnesium carbonate, calcium phosphate, and other organic matters including protein (Murakami et al. 2007). Ca replaces Na and this way Na can be eliminated as sodium sulfate (Ortiz et al. 2014) through the following reaction:



Lower levels of exchangeable sodium imply reduction of hydrolysis of clay to form hydroxides and, therefore, reduced pH. The objective was to reach pH values in the suitable range for the development of most plant species (7.5–7.8).

The addition of commercial compost to mine tailings has been shown to enhance plant growth in greenhouse trials (Schippers et al. 2000; Schroeder et al. 2005). Furthermore, compost helps prevent soil erosion and contributes to water and nutrient retention (Roongtanakiat et al. 2008).

The dose of organic amendment was calculated by the method of Hirzel (2010), which is based on the apparent density of the soil, soil organic matter content, and the moisture level of the amendment. The dose was calculated by Eqs. (1) and (2):

$$OM_d = \frac{OM_a \times AD \times SD}{0.33} \tag{1}$$

where OM<sub>d</sub> is the dose of organic matter (ton ha<sup>-1</sup>), OM<sub>a</sub> is the percentage of organic matter added, AD is the soil apparent density (g cm<sup>-3</sup>), SD is the sample depth (cm), and 0.33 is the estimated efficiency of net organic matter discharge in the soil.

$$OAD = \frac{OM_d \times 10,000}{OAD_{OM} \times (100 - H_{OAD})} \tag{2}$$

where OAD is the dose of organic amendment (ton ha<sup>-1</sup>), 10,000 is a conversion factor, OAD<sub>OM</sub> is the percentage of organic matter in the amendment, and H<sub>OAD</sub> is the percentage of moisture content in the amendment. The result provided by this method is a dose of 96.97 kg m<sup>-2</sup>.

The dose of inorganic amendment was determined by the method of Sobek et al. (1978), which theoretically estimates the maximum acidity and the neutralization potential as a result of providing the amount of CaCO<sub>3</sub> required to neutralize

concentrations of total sulfur and sulfates that can produce sulfuric acid when in contact with water. The net neutralization potential was calculated by the following equation:

$$NNP = \text{Neutralization Potential}(NP) - \text{Acid Potential}(AP) \quad (3)$$

The neutralization potential is obtained by sequential additions of hydrochloric acid to the sample to measure pH after 2, 22, and 24 h. The final result indicates the mass of  $\text{CaCO}_3$  present per ton of tailings (Lizárraga 2008). Acid potential is calculated by Eq. (4)

$$PA = 31.25(S_{\text{Total}} - S_{\text{sulfates}}) \quad (4)$$

where  $S_{\text{Total}}$  and  $S_{\text{sulfates}}$  are the percentages of total sulfur and sulfur as sulfates in the soil, respectively, and 31.25 represents the necessary stoichiometric amount of  $\text{CaCO}_3$  to neutralize the sulfur. The acid potential is expressed in kilograms required of  $\text{CaCO}_3$  per ton of tailings. The estimated amount of eggshells by this method was  $0.0405 \text{ kg kg}^{-1}$ .

### Column leaching experimental design

The design consisted of four treatments in duplicate using leaching columns: tailings without treatment (treatment A), tailings treated with  $\text{CaCO}_3$  (treatment B), tailings treated with commercial compost (treatment C), and tailings treated with both amendments (treatment D). Columns were irrigated ten times for 3 weeks with 100 mL/irrigation, and leachates were collected after each irrigation. Twelve parameters of leachate were measured ( $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , Fe,  $\text{K}^+$ , Mn, Zn,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , pH, and EC) in duplicate for each irrigation time. These parameters were chosen as they presented greater concentrations in the tailings.

Undisturbed soil columns were taken directly from mine tailings. The tool used to collect undisturbed soil columns was made of transparent methacrylate and was 0.6 m in length, with an interior diameter of 0.095 m. The height of the undisturbed soil column was 0.3 m. The remaining 0.3 m was used to add the amendments, the propylene bed, and the necessary filters and to collect leachates. Each column contained approximately 2.75 kg of tailings. The dimensions and components of the columns designed for this work are shown in Fig. 3.

For the irrigation phase, the columns were filled with water via burettes. The characteristics of the water used are presented in Table 1. The water contained significant amounts of suspended solids, making filtration necessary to avoid obstructions in the burettes. Leachates were collected in a chamber at the bottom part of the columns. The configuration and flow diagram of the eight leaching columns are shown in Fig. 4.

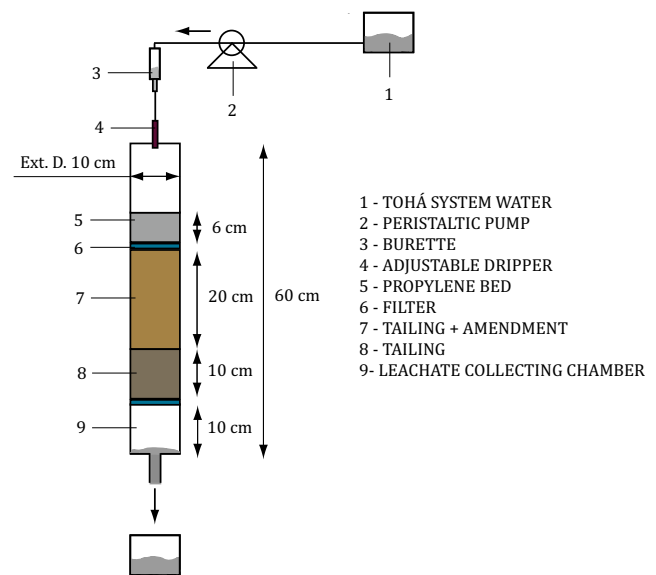


Fig. 3 Design of the experimental columns

### Statistical analysis

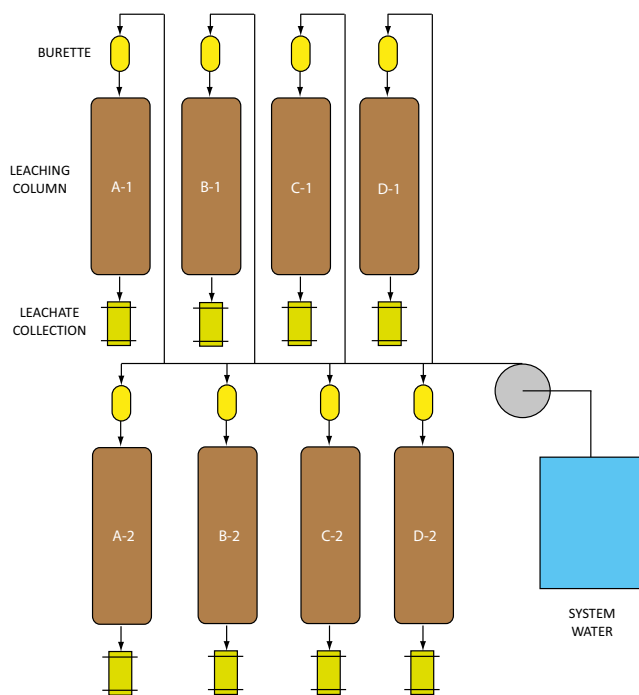
The data obtained were analyzed by two methods: (i) analysis of variance and (ii) analysis of covariance. A two-way ANOVA with two variables is provided: (1) number of irrigations and (2) amendment type. The mathematical model used to analyze the data through an ANOVA is represented by the following equation (Díaz 2009).

$$Y_{ijkl} = \mu + I_i + OA_j + IA_k + (IOA)_{ij} + (IIA)_{ik} + (OAlA)_{jk} + (IOAlA)_{ijk} + e_{ijkl} \quad (5)$$

where  $Y$  is each of the measured parameters in the leachates (pH, EC, and concentrations),  $\mu$  the mean contribution of all the parameters,  $I_i$  the effect of the number of irrigations,  $OA_j$  the effect of the organic amendment,  $IA_k$  the effect of the inorganic amendment,  $(IOA)_{ij}$  the effect of the irrigation-organic amendment interaction,  $(IIA)_{ik}$  the effect

Table 1 Chemical characteristics of the irrigation water

Parameter	Value
$\text{Cu}^{2+}$	0.12 mg L <sup>-1</sup>
Mn	101 mg L <sup>-1</sup>
Fe	0.0 mg L <sup>-1</sup>
Zn	0.02 mg L <sup>-1</sup>
$\text{SO}_4^{2-}$	75 mg L <sup>-1</sup>
$\text{NH}_4^+$	0.21 mg L <sup>-1</sup>
$\text{PO}_4^{3-}$	8.4 mg L <sup>-1</sup>
$\text{Mg}^{2+}$	30 mg L <sup>-1</sup>
$\text{K}^+$	34 mg L <sup>-1</sup>
pH	7.5
EC	1.82 dS m <sup>-1</sup>



**Fig. 4** Flow diagram of the experiments with leaching columns

of the irrigation-inorganic amendment interaction,  $(OA IA)_{jk}$  the effect of the organic amendment-inorganic amendment interaction,  $(IOA IA)_{ijk}$  the effect of the irrigation-organic amendment-inorganic amendment interaction, and  $e_{ijkl}$  the effect of random error. To develop the analysis, several hypotheses were taken into account:

$$H_0 : \mu_{Ii} = \mu \quad H_0 : \mu_{OAj} = \mu_e \quad H_0 : \mu_{IAk} = \mu_e$$

$$H_1 : \mu_{Ii} \neq \mu_e \quad H_1 : \mu_{OAj} \neq \mu_e \quad H_1 : \mu_{IAk} \neq \mu_e$$

$$H_0 : \mu_{(IOA)ij} = \mu_e \quad H_0 : \mu_{(IIA)ik} = \mu_e$$

$$H_1 : \mu_{(IOA)ij} \neq \mu_e \quad H_1 : \mu_{(IIA)ik} \neq \mu_e$$

$$H_0 : \mu_{(OALA)_{jk}} = \mu_e \quad H_0 : \mu_{(IOAIA)_{ijk}} = \mu_e$$

$$H_1 : \mu_{(OALA)_{jk}} \neq \mu_e \quad H_1 : \mu_{(IOAIA)_{ijk}} \neq \mu_e$$

To simplify the analysis, four levels were considered for irrigation: (i) initial irrigation or number 1, (ii) irrigation number 4, (iii) irrigation number 7, and (iv) irrigation number 10. With this, it was possible to measure the tendencies of the effects of the different irrigations on the measured parameters. Therefore, four of the ten measured irrigations were considered. For the amendments, two levels were considered: presence and absence. Moreover, the results of the two replicates were taken into account to determine error. The analysis was carried out considering a confidence interval of at least 95 %. The ANOVA was developed with a MS Excel template created for this kind of two-factor analysis.

The objective of the analysis of covariance was to establish the possible relationships between two parameters measured in the leachates. This study was developed separately for all the treatments; for example, the Cu-pH relationship was

analyzed four times (treatments A, B, C, and D). The basis of this analysis is the calculation of the Pearson correlation coefficient.

## Results and discussions

### Comparison of tailings and surrounding soil

The tailings and surrounding soil were compared to identify the main differences and to select the parameters for analysis for our work. Table 2 presents the statistical summary of the analysis of the tailings divided by depths. Table 3 shows the statistical summary of the parameters measured in the surrounding soil. The comparative analysis of parameters between the tailings and the surrounding soil is described below.

#### Aluminum

The concentration of Al in the tailings was twice as high as in the surrounding soil. Nevertheless, there was no risk of toxicity because aluminum becomes toxic in soils with pH below 5.0 (Plaster 2000) and the pH levels in the tailings and soil were above this level.

#### Arsenic

The concentration of As was higher in the surrounding soil (21.69 mg/kg) than in the tailings (average value of the three depths 3.663 mg/kg); this is explained by the concentration of As in sulfide ores, which is lower than that of surrounding sites due to the mineralogy of the ores.

#### Boron

As with arsenic, the surrounding soil presented higher concentrations of B. This element can be a problem in arid regions with low precipitation since rainwater regulates the amount of B in the soil. In addition, the concentration of B in irrigation water must be controlled to avoid excessive levels of this element (Reid 2010).

#### Cadmium

The maximum value of Cd in the surrounding soil was 0.5993 mg/kg, which was lower than the levels in the three column depths. Cadmium concentrations need to be controlled because Cd can affect the plant growth (Sanitá Di Toppi and Gabbriellini 1999; Benavides et al. 2005) and harmful to the environment.

**Table 2** Descriptive statistics of chemical parameters of the tailing used in this study at different depths: 0–10, 10–20, and 20–30 cm

Parameter	Depth 0–10 cm				Depth 10–20 cm				Depth 20–30 cm			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
Al (mg kg <sup>-1</sup> )	23841	–	23841	23841	19313	1630.9	18052	21155	22855	–	22855	22855
As (mg kg <sup>-1</sup> )	3.627	–	3.627	3.627	3.216	0.488	2.830	3.764	4.145	–	4.145	4.145
B (mg kg <sup>-1</sup> )	64.1	–	64.1	64.1	87.4	5.79	83.7	94.1	57.3	–	57.3	57.3
Ca (mg kg <sup>-1</sup> )	279.7	25.41	250.1	293.3	231.8	8.50	163.7	285.6	233.7	7.23	175.2	285.1
Cd (mg kg <sup>-1</sup> )	1.339	0.912	0.099	2.596	1.283	0.669	0.599	2.298	1.936	0.962	0.698	3.900
Cl <sup>-</sup> (mg kg <sup>-1</sup> )	8774	3927.2	2746	9826	7696	1728.6	2161	10001	7849	2802	2578	9611
Cr (mg kg <sup>-1</sup> )	2.894	–	2.894	2.894	8.869	2.583	5.887	10.38	5.898	–	5.898	5.898
Cu (mg kg <sup>-1</sup> )	10571	1942.3	1008	14426	12061	2483	8231	16296	11080	2327.1	8181	14171
EC (dS m <sup>-1</sup> )	37.50	10.39	14.30	39.90	27.60	9.23	16.40	40.10	38.10	12.03	15.30	39.60
Fe (mg kg <sup>-1</sup> )	35488	2889.2	31278	41923	34021	3307.9	19236	40489	34794	5143.9	23457	41652
K (mg kg <sup>-1</sup> )	18.04	–	18.04	18.04	59.30	8.38	52.05	68.47	45.04	–	45.04	45.04
Mg (mg kg <sup>-1</sup> )	106.6	60.19	45.78	126.5	68.52	11.35	30.13	99.2	485.5	6.12	25.81	123.0
Mn (mg kg <sup>-1</sup> )	322.8	76.125	215.8	441.9	341.6	69.4	227.4	445.4	381.2	77.7	264.9	467.8
Mo (mg kg <sup>-1</sup> )	133.7	–	133.7	133.7	85.39	10.99	78.12	98.04	59.98	–	59.98	59.98
Na (mg kg <sup>-1</sup> )	3270.1	1017.08	1639	6086	2484.2	1257.5	1732	4441	3180.5	1208.4	1950	5976
Pb (mg kg <sup>-1</sup> )	75.65	–	75.65	75.65	182.4	34.5	146.6	215.4	107.3	–	107.3	107.3
pH	8.27	0.232	8.23	8.52	8.39	0.16	8.27	8.45	8.40	0.14	8.25	8.47
Sat. water (%)	64.9	1.37	63.1	68.4	68.5	2.8	63.1	74.0	65.9	1.1	63.3	67.3
SO <sub>4</sub> <sup>2-</sup> (mg kg <sup>-1</sup> )	3382.6	703.34	2459	3939	3303.6	907.9	2780.1	4439	3720	2557.5	1638	4441
Zn (mg kg <sup>-1</sup> )	296.7	7.23	287.2	302.3	300.4	9.33	108.6	301.9	342.9	1.83	288.6	306.6

Mean average value, SD standard deviation, Min minimum value, Max maximum value

### Calcium

Calcium affects soil acidity (Giesler et al. 1998). It is generally added to the soil as gypsum to recover sodic-saline and sodic soils (Marschner 1995). Calcium accumulates in the surface layer of tailings (0–10 cm). We found the concentration in the tailings higher than in the surrounding soils (pH ≈8 versus pH ≈6.6 in the soils).

### Chloride

Chlorine is an essential micronutrient for plants, generally present as chloride ions (Cl<sup>-</sup>) (Marschner 1995). The concentration in the tailings was several orders of magnitude greater than in the soil.

### Chromium

Chromium concentrations in the second depth (10–20 cm) and the soil were quite similar. However, pH in tailings tends to be alkaline so that chromium become highly mobile (Zalidis et al. 1999) and can take the form of hexavalent Cr, which is assumed to be extremely toxic for the environment (Marsh and Mcinerney 2001).

### Copper

The concentration of Cu in the tailings was 30 times as high as in the surrounding soil. Copper is an important micronutrient for plants, since it is part of some metalloenzymes and proteins involved in electron transport and redox reactions (Cervantes and Gutierrez-Corona 1994).

### Electrical conductivity

Electrical conductivity is an important parameter to know the properties of the soil and water, as it is an indicator of salinity. An increase in salinity implies greater mobility of metals (García et al. 2009). The soil had a mean EC value of 8.23 dS m<sup>-1</sup>, while in the tailings values ranged between 23.6 and 42.1 dS m<sup>-1</sup>.

### Iron

Iron concentrations were higher in the tailings. Iron is an essential micronutrient for plants, but it is important to know the level of oxidation since Fe is toxic when the ions are bivalent (Bornemisza 1982).

**Table 3** Descriptive statistics of chemical parameters of the surrounding soil

Parameter	Mean	SD	Min	Max
Al (mg kg <sup>-1</sup> )	10115	1364.6	8410	11640
As (mg kg <sup>-1</sup> )	21.69	2.243	18.25	24.15
B (mg kg <sup>-1</sup> )	70.5	39.04	25.9	125
Ca (mg kg <sup>-1</sup> )	105.85	32.43	78.84	157.50
Cd (mg kg <sup>-1</sup> )	0.3789	0.1785	0.1994	0.5993
Cl <sup>-</sup> (mg kg <sup>-1</sup> )	399.04	253.69	144.68	714.50
Cr (mg kg <sup>-1</sup> )	7.574	2.417	4.078	10.830
Cu (mg kg <sup>-1</sup> )	395.1	141.4	283.8	638.4
EC (dS m <sup>-1</sup> )	8.23	3.87	4.57	14.00
Fe (mg kg <sup>-1</sup> )	19954	2133.8	17325	22175
K (mg kg <sup>-1</sup> )	14.851	8.634	6.957	26.250
Mg (mg kg <sup>-1</sup> )	20.22	3.53	16.09	23.75
Mn (mg kg <sup>-1</sup> )	773.3	128.2	661.2	987.2
Mo (mg kg <sup>-1</sup> )	11.004	5.701	3.282	18.540
Na (mg kg <sup>-1</sup> )	210.49	144.64	77.64	423.90
Pb (mg kg <sup>-1</sup> )	49.44	9.09	37.26	56.74
pH	6.60	0.254	6.18	6.84
Water sat. (%)	25.4	5.39	20.7	33.8
SO <sub>4</sub> <sup>2-</sup> (mg kg <sup>-1</sup> )	567.4	140.4	425.0	744.8
Zn (mg kg <sup>-1</sup> )	97.57	11.76	82.47	114.70

Mean average value, SD standard deviation, Min minimum value, Max maximum value

*Potassium*

Potassium is one of the principal nutrients for plants, together with N and P. Nevertheless, there is a shortage of K in many regions of the world (Dobermann et al. 1998; Smaling 1998; Wang et al. 2008; Liu et al. 2009). The highest K concentrations in the tailings were located in the second depth. Therefore, if phytoremediation is applied, it is not necessary to add amendments with high concentrations of K. Mobility of K can be influenced by the degrees of leaching and soil adsorption (Johnston et al. 1993; Liao et al. 2013).

*Magnesium*

The concentrations of Mg measured in the tailings were 11 times as high as in the soil. It is important to evaluate the behavior of Mg since an excess of this element can affect the mobility of potassium (Jalali 2008) and also induces P availability (Shariatmadari and Mermut 1999).

*Manganese*

Manganese is an essential trace element for plant growth. The concentrations were higher in the surrounding soil than in the tailings.

*Molybdenum*

Molybdenum is a required micronutrient for plants and animals (Sequi 1973; O’Connor et al. 2001). As expected, concentrations in the tailings were higher than in the soil. For alkaline soils like the tailings under study, Mo is related to Ca (Essington 1990).

*Sodium*

The presence of Na in soils is very important because high concentrations can be toxic for plants (Delvaux 1995; Vargas and Rodríguez 2000). Soils in arid climates like northern Chile are rich in salinity and sodicity (Suárez 2001; Qadir et al. 2006, 2007). As expected, the concentrations in the tailings were several times as high as in the surrounding soil, since the tailings were classified as extremely sodic.

*Lead*

The Pb concentration in the tailings was almost three times as high as in the soil. It is very important to monitor the presence of Pb, given the potential risk to the environment and human health (Hettiarachchi et al. 2000; Yang et al. 2001).

*Zinc*

The maximum concentration of Zn was located in the lowest layer, while the surrounding soil presented smaller quantities. In alkaline soils like that of the tailings, Zn is absorbed in higher proportion by the soil (Alloway 2008).

*Sulfates*

Sulfates have the opposite effect of carbonates, acidifying the soil (Urbano 2001). In the tailings, the mean level was 3500 mg/kg, while the surrounding soil had lower concentrations, with a mean value of 567.4 mg/kg.

*Water saturation*

As expected, the water saturation was higher in the tailings than in the surrounding soil, which is normal for the arid climate of the Antofagasta Region.

*pH*

Most metals tend to be more available with low pH, with the exception of V, As, Mo, Se, and Cr, which are more available with basic pH. Most metals are less mobile under basic conditions because they precipitate as hydroxides (Cappuyans and Swennen 2008). The tailings presented

alkaline characteristics (pH  $\approx$ 8.4), while the surrounding soil was slightly acidic (pH  $\approx$ 6.6).

### Analysis of leachate

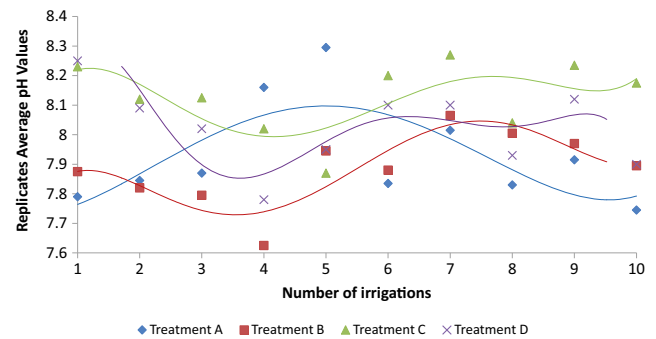
The results of heavy metals, pH, and EC in leachate are presented in Figs. 5, 6, 7, 8, 9, 10, and 11 depending on the number of irrigations.

#### pH

- (i) Number of irrigations, I: as shown in Fig. 5, no definite tendency was observed, given that pH values varied in most experiments. However, by the seventh irrigation, pH values began to stabilize in treatments C and D, while they decreased in treatment B.
- (ii) Organic amendment, OA: pH values were higher in the treatments with the organic amendment C and D than in the other treatments, with the exception of treatment A after the fourth and fifth irrigations. This result is in line with that of Odlare et al. (2008), where the increase in pH was explained by the release of ammonia.
- (iii) Number of irrigations-inorganic amendment interaction, I IA: pH values of treatments A (control treatment) and B were similar, although treatment B presented less variability. The maximum value was reached by the seventh irrigation, after which pH started to decrease gradually. For the control treatment, once the maximum value was reached, a clear tendency could not be observed. As a result, the addition of the amendment avoided a sharp decrease in pH.
- (iv) Number of irrigations-organic amendment interaction, I OA: as noted above, treatments with organic amendments presented the highest pH values. The pH values were highly variable, ranging from the minimum values after the fifth irrigation to the maximum value after the seventh irrigation.
- (v) Number of irrigations-organic amendment-inorganic amendment interaction, I OA IA: pH values for treatment D were slightly lower than for the organic amendment treatment (C). The behavior during the first irrigation was more irregular than the other treatments, while after the fifth irrigation, the pH level stabilized around 8.1.

#### Electrical conductivity

- (i) Number of irrigations, I: as shown in Fig. 6, EC decreased in a linear manner throughout the experiment, which was expected as salts are extracted from the soils with irrigation.

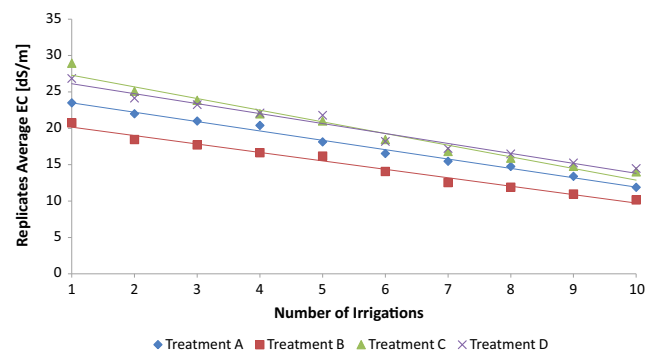


**Fig. 5** Effect of treatments and irrigations on pH from leachate collected

- (ii) Inorganic amendment, IA: leaching from the treatments with inorganic amendment (B) presented lower EC values than the other treatments. This is inconsistent with the hypotheses that salts in soils are easily removed as sodium sulfate through leaching when calcium carbonate is added.
- (iii) Organic amendment, OA: leaching in treatments C and D presented the highest EC values. Treatment C showed the most significant decrease in this parameter (approximately  $15 \text{ dS m}^{-1}$  throughout the experiment), while the other treatments show similar decreases. The compost used as organic amendment enhanced porosity in contrast to the other amendment, resulting in a more effective wash and consequently a more pronounced decrease in EC.
- (iv) Inorganic amendment-organic amendment interaction, IA OA: as noted above, treatment C (only the organic amendment) presented the highest level of EC, while the presence of the inorganic amendment reduced the variations in EC.

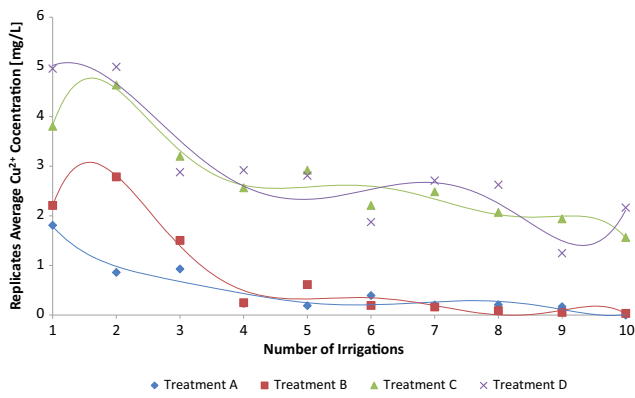
#### Copper

- (i) Number of irrigations, I: the concentration of  $\text{Cu}^{2+}$  decreases over the course of the four treatments. This can be explained by the initially high levels of salinity in the



**Fig. 6** Effect of treatments and irrigations on EC from leachate collected





**Fig. 7** Effect of treatments and irrigations on Cu<sup>2+</sup> concentrations from leachate collected

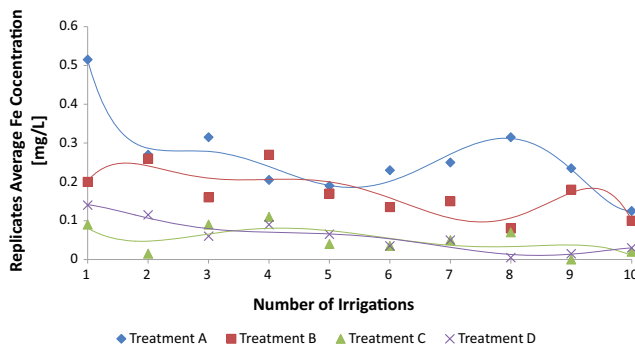
tailings, which was reduced, along with copper mobility, by the number of irrigations (Fig. 7).

- (ii) Organic amendment, OA: the two treatments based on organic amendment presented the highest concentrations in the leachate. Copper mobility did not decrease with the presence of organic matter, but rather increased, as was reported by Sawhney et al. (1994) and Kaschl et al. (2002).

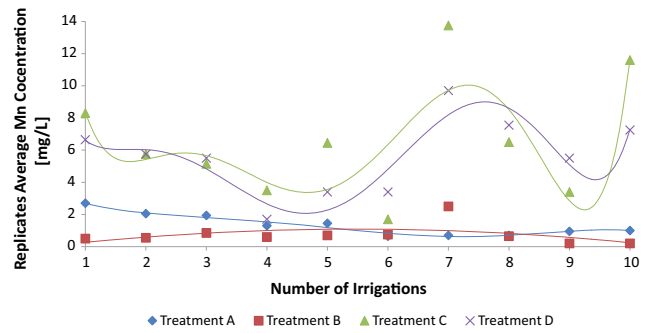
Organic matter can react with metals to form charge-transfer complexes and chelates that can move easily throughout the profile. The formation of organometallic compounds facilitates solubility, availability, and dispersion. The stability constants of chelates formed by organic matter and metals in the order of Cu > Fe = Al > Mn = Co > Zn. The maximum amount of any metal that can be bound is approximately the number of carboxyl groups of the chelating agent (Alloway 1995).

*Iron*

- (i) Number of irrigations: as noted above with Cu, the concentration of Fe decreased in all the treatments due to



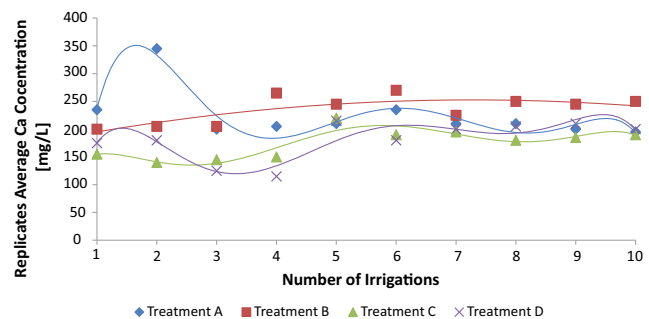
**Fig. 8** Effect of treatments and irrigations on Fe concentrations from leachate collected



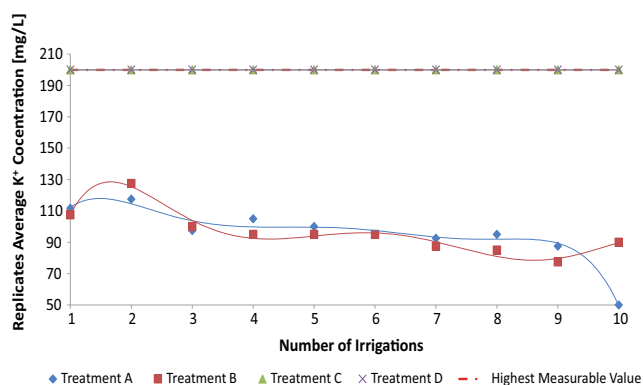
**Fig. 9** Effect of treatments and irrigations on Mn concentrations from leachate collected

irrigation, the decrease in treatment A being the most pronounced (Fig. 8).

- (ii) Inorganic amendment, IA: the concentrations of Fe in leachate from treatment B (only inorganic amendment) were lower than from treatment A (only tailings), which can be explained by the addition of calcium carbonate since this element is less mobile and available in calcareous and alkaline soils (Arizmendi et al. 2011).
- (iii) Organic amendment, OA: for treatment C, the concentrations were lower than for treatments A and B. Acevedo et al. (2004) reported that Fe is retained in aerobic conditions and precipitates as Fe<sub>2</sub>O<sub>3</sub>.nH<sub>2</sub>O if the soil pH is higher than 3.5.
- (iv) Inorganic amendment-organic amendment interaction, IA OA: treatment A presented higher concentrations of Fe than treatment C. Both the addition of organic and inorganic amendments immobilized Fe in the soil, indicating a synergistic effect of the two amendments.
- (v) Number of irrigations-inorganic amendment-organic amendment interactions, I IA OA: treatment D presented a more uniform tendency of decreasing Fe concentrations than the other treatments. In addition to the synergistic effect of the amendments, the reduction in salinity due to irrigation washing out the soil must be taken into account.



**Fig. 10** Effect of treatments and irrigations on Ca<sup>2+</sup> concentrations from leachate collected



**Fig. 11** Effect of treatments and irrigations on  $K^+$  concentrations from leachate collected

### Manganese

As shown in Fig. 9, Mn concentrations in treatments C and D were higher than in treatment A. However, this result contradicts those of Fassbender and Roldan (1973), who found that Mn adsorption increases with the presence of organic matter. Furthermore, the alkaline characteristics of the tailings result in Mn taking the form of tetravalent Mn, with low mobility and bioavailability.

### Calcium

- (i) The number of irrigations: the concentration of  $Ca^{2+}$  increased slightly in all the treatments except treatment A (Fig. 10) which was unexpected since  $Ca^{2+}$  is usually related to EC.
- (ii) Organic amendment, OA: concentrations measured in leaching from treatment C were lower than for treatment A. The addition of the organic amendment increased the cation-exchange capacity of the soils, stimulating greater  $Ca^{2+}$  retention.
- (iii) Number of irrigations-inorganic amendment interaction, IIA: the concentration of  $Ca^{2+}$  in treatment B increased with irrigation and the addition of inorganic amendment, which was expected.
- (iv) Number of irrigations-inorganic amendment-organic amendment interaction, IIA OA: the behavior of treatments C and D was similar, but the leaching concentrations were slightly higher in treatment D, which could have been due to the inorganic amendment.

### Potassium

- (i) Number of irrigations, I: as shown in Fig. 11, K levels decreased in treatments A and B, but increased in treatment B after the last irrigation.

- (ii) Organic amendment, OA: concentrations in leachate from treatments with the organic amendments are beyond the detection limit. Comparing this to the mean values of the other treatments (125 mg/L) reveals a clear effect of the organic amendment on the concentration of  $K^+$ .
- (iii) Number of irrigations-inorganic amendment interaction, IIA: the concentrations of treatments A and B were very similar until after the last irrigation, when the concentration of potassium increased in treatment B and decreased sharply in treatment A.

### Zinc and magnesium

The measurements of Zn and Mg were beyond the detection range of our equipment, in the case of Zn below (0.01 mg/L) and in the case of Mg above (150 mg/L) the detection limits. Consequently, no statistical analysis was made for these elements.

The low concentration of zinc was due to the alkaline character of the tailings and the addition of calcium carbonate as an inorganic amendment. The high concentration of Mg can be explained by the high cation-exchange capacity and the amendments employed.

### Analysis of variance

The analysis of variance, at a significance level of 5 %, provided the following findings. The number of irrigations and the inorganic amendment and the organic amendment significantly affected EC, with  $p$  values of 0, 0.014, and 0.01, respectively. The concentration of copper is significantly affected by the number of irrigations, the inorganic amendment, the organic amendment, and the interaction between the two amendments, providing  $p$  values of 0, 0.006, 0, and 0.014, respectively. The organic amendment affected the concentrations of Mn ( $p$  value of 0.003) and Fe (0.046). The effects of the inorganic amendment, the organic amendment, and the interaction between them were found for sulfate concentrations in leachate, with  $p$  values of 0.001, 0.002, and 0.001 respectively. No statistical evidence was found for the influence of the number of irrigations and the application of the amendments for the remaining parameters.

### Analysis of covariance

The results of the analysis of covariance are presented to evaluate the interactions among the physicochemical parameters for the four treatments. The criterion to define significant relationship among the parameters was a Pearson coefficient greater than or equal to an absolute value of 0.80. Tables 4, 5, 6, and, 7 show the results of

**Table 4** Pearson correlation matrix for treatment A

Variable	Correlations											
	pH	EC	Cu <sup>2+</sup>	Mn	Fe	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub> <sup>-</sup>	Zn	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>
pH	1.00											
EC	0.12	1.00										
Cu <sup>2+</sup>	-0.35	(0.81)	1.00									
Mn	-0.10	(0.85)	(0.88)	1.00								
Fe	-0.34	0.63	(0.89)	0.66	1.00							
PO <sub>4</sub> <sup>3-</sup>	0.47	(0.86)	0.45	0.60	0.30	1.00						
NO <sub>3</sub> <sup>-</sup>	-0.56	(-0.80)	-0.41	-0.70	-0.23	(-0.88)	1.00					
Zn	0.61	0.25	-0.21	-0.01	-0.25	0.66	-0.54	1.00				
SO <sub>4</sub> <sup>2-</sup>	0.54	0.75	0.30	0.60	0.10	(0.86)	(-0.96)	0.50	1.00			
Ca <sup>2+</sup>	-0.24	0.47	0.37	0.41	0.17	0.27	-0.23	-0.19	0.29	1.00		
NH <sub>4</sub> <sup>+</sup>	-0.29	-0.40	-0.19	-0.58	-0.01	-0.51	0.72	-0.41	-0.63	-0.28	1.00	
K <sup>+</sup>	0.28	(0.82)	0.58	0.53	0.58	0.73	-0.63	0.21	0.61	0.51	-0.16	1.00

Correlations greater than an absolute value of 0.80 are shown in parentheses

the analysis of covariance, using the Pearson coefficient, for all the treatments.

*pH*

The analysis of covariance for treatments A, B, and C showed no significant relationship between pH and any measured parameter. However, there was a directly proportional relationship between pH and NO<sub>3</sub><sup>-</sup> concentration in treatment D. This result is in line with that provided by Kemmitt et al. (2005), who stated that when pH decreases, nitrate leaching is reduced.

*Electrical conductivity*

The analysis of covariance identified several parameters as significantly related to EC for treatment A. A directly proportional relationship was found with the concentrations of Cu<sup>2+</sup>, Mn, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, and K<sup>+</sup>. Acosta et al. (2011) and Zhao et al. (2013) determined that the mobilities of Cu and Mn are affected by soil salinity. For treatment B, a direct proportional relationship was found between EC and Cu<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> concentrations. For treatment C, a direct proportional relationship was identified with the concentrations of Cu<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup>. Regarding treatment D, a directly proportional relationship was found for the concentrations of Cu<sup>2+</sup> and Fe. The

**Table 5** Pearson correlation matrix for treatment B

Variable	Correlations											
	pH	EC	Cu <sup>2+</sup>	Mn	Fe	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub> <sup>-</sup>	Zn	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>
pH	1.00											
EC	-0.53	1.00										
Cu <sup>2+</sup>	-0.30	(0.83)	1.00									
Mn	0.40	-0.06	-0.13	1.00								
Fe	-0.66	0.66	0.54	-0.10	1.00							
PO <sub>4</sub> <sup>3-</sup>	-0.30	(0.82)	0.75	-0.07	0.51	1.00						
NO <sub>3</sub> <sup>-</sup>	0.15	-0.65	-0.47	-0.31	-0.47	-0.37	1.00					
Zn	0.19	0.46	0.41	0.31	0.14	0.76	-0.18	1.00				
SO <sub>4</sub> <sup>2-</sup>	-0.20	0.78	0.43	0.22	0.32	0.76	-0.51	0.73	1.00			
Ca <sup>2+</sup>	-0.07	-0.56	(-0.81)	-0.14	-0.25	-0.55	0.40	-0.56	-0.33	1.00		
NH <sub>4</sub> <sup>+</sup>	0.31	-0.36	-0.20	0.47	-0.01	-0.23	-0.19	-0.24	-0.42	0.15	1.00	
K <sup>+</sup>	-0.44	0.78	(0.91)	-0.11	0.59	0.67	-0.33	0.23	0.34	-0.57	-0.12	1.00

Correlations greater than an absolute value of 0.80 are shown in parentheses

**Table 6** Pearson correlation matrix for treatment C

Variable	Correlations											
	pH	EC	Cu <sup>2+</sup>	Mn	Fe	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub> <sup>-</sup>	Zn	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>
pH	1.00											
EC	-0.12	1.00										
Cu <sup>2+</sup>	-0.09	(0.88)	1.00									
Mn	0.27	-0.18	-0.08	1.00								
Fe	-0.23	0.51	0.17	-0.05	1.00							
PO <sub>4</sub> <sup>3-</sup>	-0.07	(0.85)	(0.85)	-0.02	0.26	1.00						
NO <sub>3</sub> <sup>-</sup>	0.01	-0.08	-0.31	0.32	0.17	-0.02	1.00					
Zn	0.13	-0.43	-0.44	0.47	-0.31	-0.16	0.42	1.00				
SO <sub>4</sub> <sup>2-</sup>	0.01	-0.08	-0.31	0.32	0.17	-0.02	(1.00)	0.42	1.00			
Ca <sup>2+</sup>	-0.13	-0.69	-0.66	0.30	-0.50	-0.64	0.35	0.36	0.35	1.00		
NH <sub>4</sub> <sup>+</sup>	0.13	-0.56	-0.32	-0.01	-0.38	-0.32	-0.26	-0.25	-0.26	0.26	1.00	
K <sup>+</sup>	0.69	-0.33	-0.33	0.42	-0.17	-0.44	-0.19	0.29	-0.19	0.20	-0.06	1.00

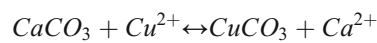
Correlations greater than an absolute value of 0.80 are shown in parentheses

application of amendments significantly affected the types of ions present, with a direct effect on EC.

#### Copper

The analysis of covariance of treatment A provided an opportunity to identified directly proportional relationships between the concentrations of Cu<sup>2+</sup>/Fe and Cu<sup>2+</sup>/Mn, which can be explained due to the effect of the salinity of the soil on metal mobility. The cations associated with the salts can replace heavy metals in adsorption sites. For treatment B, directly proportional relationships

were found between EC and the concentration of K<sup>+</sup>. Furthermore, an inversely proportional relationship with the concentration of Ca<sup>2+</sup> was defined, which could be explained by the following reaction (Ponizovsky et al. 2007)



For treatment C, a directly proportional relationship was found between EC and PO<sub>4</sub><sup>3-</sup> concentrations. Chen et al. (2003) reported the same relationship. For treatment D, a directly proportional relationship between EC and Fe was identified.

**Table 7** Pearson correlation matrix for treatment D

Variable	Correlations											
	pH	EC	Cu <sup>2+</sup>	Mn	Fe	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub> <sup>-</sup>	Zn	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>
pH	1.00											
EC	0.12	1.00										
Cu <sup>2+</sup>	0.10	(0.83)	1.00									
Mn	0.38	-0.31	0.10	1.00								
Fe	0.12	(0.91)	(0.89)	-0.19	1.00							
PO <sub>4</sub> <sup>3-</sup>	0.16	0.70	0.52	-0.39	0.53	1.00						
NO <sub>3</sub> <sup>-</sup>	0.74	-0.08	0.12	0.51	0.10	-0.07	1.00					
Zn	-0.58	-0.16	-0.15	-0.32	0.03	-0.09	-0.21	1.00				
SO <sub>4</sub> <sup>2-</sup>	-0.01	0.10	-0.17	-0.54	0.01	-0.17	0.00	-0.04	1.00			
Ca <sup>2+</sup>	0.30	-0.48	-0.16	0.49	-0.37	-0.35	0.42	-0.37	-0.07	1.00		
NH <sub>4</sub> <sup>+</sup>	-0.29	0.10	0.16	-0.26	0.09	-0.07	-0.41	-0.35	0.18	0.17	1.00	
K <sup>+</sup>	-0.05	-0.31	-0.34	-0.29	-0.39	0.36	0.05	0.00	-0.05	0.15	0.08	1.00

Correlations greater than an absolute value of 0.80 are shown in parentheses

### Iron

The analysis of covariance for the treatment A showed a direct proportional relationship between the concentrations of Fe and  $\text{Cu}^{2+}$ , which can be explained by reduced soil salinity owing to irrigation. No significant relationships were found between the concentration of Fe and any measured parameters for treatments B and C. A direct relationship with EC and  $\text{Cu}^{2+}$  was identified for treatment D.

### Manganese

For treatment A, the analysis of covariance found a direct proportional relationship between Mn-EC, Mn- $\text{Cu}^{2+}$ , and Mn-Fe due to the effect of salinity on metal mobility. No significant relationships were found between manganese concentrations and the measured parameters in treatments B, C, and D.

### Calcium

The analysis of covariance for treatment A identified a direct proportional relationship with the concentration of  $\text{K}^+$ . For treatment B, inverse proportional relationships were found with  $\text{Ca}^{2+}$ -EC and  $\text{Ca}^{2+}$ - $\text{Cu}^{2+}$ . The same relationship with the concentration of  $\text{Cu}^{2+}$  was obtained for treatment C. No significant relationships were found for treatment D.

### Potassium

The analysis of covariance of treatments A and B identified direct proportional relationships between  $\text{K}^+$ -EC,  $\text{K}^+$ - $\text{Cu}^{2+}$ ,  $\text{K}^+$ - $\text{PO}_4^{3-}$ , and  $\text{K}^+$ - $\text{Ca}^{2+}$  concentrations. Zhang et al. (2009) reported the relationship between the concentration of K and EC. No significant relationships were found for treatments C and D.

## Conclusions

The physicochemical properties of the tailings, such as concentrations of metals, pH, and EC, were analyzed and compared to those of the surrounding soil. Metal concentrations were higher in the tailings than in the soil, with the exception of As, Mn, and B. The greatest differences in concentrations were for Cu, Fe, and Mg. Due to the salinity of the tailings, Cu, Fe, and Mn can be expected to be highly mobile. On the other hand, because pH is alkaline, aluminum concentrations are unlikely to be toxic to plants, but can stimulate the mobility of other toxic metals, such as Cr.

With respect to the effect of the amendments on the leachates collected underneath the columns,  $\text{Cu}^{2+}$  was found in significantly higher concentrations than in the control.

Calculations of concentrations showed that the concentration in average of  $\text{Cu}^{2+}$  in tailing treated with  $\text{CaCO}_3$ , tailing treated with compost, and tailing treated with both amendments were 0.93, 2.22, and 2.63 mg/L, respectively, compared to 0.51 mg/L. In contrast, Fe was found in significantly lower concentrations than in the control, in average adding  $\text{CaCO}_3$  or compost or both amendments were 0.12, 0.03, and 0.04 mg/L, respectively, compared to 0.21 mg/L. This indicated that the mobility of Fe decreased in the leachate and the bioavailability of  $\text{Cu}^{2+}$  increased due to effects of the amendments.

Leachates from tailings amended with compost showed a slight increase in the pH in the range of 7.8 to 8.2. These leachates presented the highest EC values. Moreover, EC tended to decrease with the number of irrigations. The leachates from tailings amended with  $\text{CaCO}_3$  showed the lowest EC values. The ANOVA, at a significance level of 5 %, showed that the number of irrigations and the amendments had a significant influence on EC. The inorganic amendment was the least effective treatment in eliminating salts. Therefore, this amendment is not useful for decreasing salinity in tailings.

To determine the interaction among the parameters measured, a criterion of Pearson coefficient greater or equal than an absolute value of 0.80 was employed. Direct proportional relationships between EC- $\text{Cu}^{2+}$ , EC-Mn, EC- $\text{PO}_4^{3-}$ , EC- $\text{K}^+$ ,  $\text{Cu}^{2+}$ -Mn,  $\text{Cu}^{2+}$ -Fe, and  $\text{PO}_4^{3-}$ - $\text{SO}_4^{2-}$  were found, while inverse relationships between EC- $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ - $\text{NO}_3^-$ , and  $\text{NO}_3^-$ - $\text{SO}_4^{2-}$  were identified. The relationship between EC and metals stimulates the mobility of  $\text{PO}_4^{3-}$ , Mn,  $\text{K}^+$ , and  $\text{Cu}^{2+}$ . With the application of  $\text{CaCO}_3$  or compost, a positive relationship between EC- $\text{Cu}^{2+}$  and EC- $\text{PO}_4^{3-}$  was found; however, the application of both amendments showed a direct relationship between EC- $\text{Cu}^{2+}$ , EC-Fe, and  $\text{Cu}^{2+}$ -Fe. Moreover, direct relationships between  $\text{Cu}^{2+}$ - $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$ - $\text{SO}_4^{2-}$  were observed in the tailing treated with organic amendment. Regarding the tailing treated with  $\text{CaCO}_3$ , from the results provided by the correlation matrix, it can be observed that the mobility of  $\text{Cu}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{K}^+$  increased with the increase of EC.

**Acknowledgments** This study was carried out in the framework of a CORFO-INNOVA project (08CM01-05), titled “Integrated development of magneto-chemical technologies and phytotechnologies applied to the remediation of heavy metals in mining environmental liability development”.

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