Copper distribution in leaves and roots of plants growing on a copper mine-tailing storage facility in northern Chile

Distribución de cobre en hojas y raíces de plantas que crecen sobre relaves mineros de cobre en el norte de Chile

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ABSTRACT

In a copper mine-tailing afforested we characterized the physicochemical properties of the substrate at vegetated and non-vegetated patches. We studied the accumulation of copper in roots and leaves of the species present at the site, to evaluate their phytoextraction and/or phytostabilization potential. The non-vegetated mine-tailing substrate showed a high content of metals, mainly copper (> 2.5 g kg^{-1}), a pH 7.4, high content of salts and 5.0 % organic matter. Vegetated patches at the tailing showed similar characteristics of pH, salts and organic matter content, and showed a total copper concentration lower than the content found at the non-vegetated patches. Nine plant species present at the site were screened for copper accumulation and distribution in roots and leaves, and potential for copper phytoextraction or phytostabilization was suggested. The native species *Schinus polygamus* and *Atriplex deserticola,* accumulated over 1.2 g kg^{-1} copper in their leaves, showing that they are pseudometallophytes for the metal. Five of the nine plant species studied were considered suitable for phytoextraction procedures and four were apt for phytostabilization of copper polluted sites. By making a screening of species growing on a copper polluted site, we were able to select plants adapted to semi-arid environmental conditions and suitable for mine-tailings remediation purposes.

Key words: copper, phytoextraction, phytostabilisation, remediation, native plants.

RESUMEN

En un tranque de relaves previamente forestado, se realizó una caracterización fisicoquímica del sustrato en sectores vegetados y no vegetados. Se estudió la acumulación de cobre en raíces y hojas de las especies presentes en el sitio de trabajo, con el objeto de evaluar su potencial fitoextractor y fitoestabilizador. El sustrato del sector no vegetado presentó un pH 7,4; altos contenidos de sales y 5,0 % de materia orgánica, además de un alto contenido de metales pesados, principalmente cobre (> 2,5 g kg^{-1}). Los sectores vegetados del tranque de relaves presentaron características similares en cuanto a pH, sales y contenido de materia orgánica, pero tenían concentraciones de cobre menores a las determinadas en los sectores no vegetados. Nueve especies presentes en el sitio fueron analizadas para determinar la acumulación de cobre en raíces y en hojas, y se sugirió la capacidad fitoextractora o fitoestabilizadora de cada especie. Las especies endémicas S*chinus polygamus* y *Atriplex deserticola* acumularon sobre 1,2 g kg^{-1} de cobre en sus hojas, presentando características de seudometalófitas para el metal. Cinco de las nueve especies estudiadas fueron consideradas adecuadas para procedimientos de fitoextracción de cobre, y cuatro especies mostraron capacidad para fitoestabilizar suelos contaminados con cobre. Mediante la identificación de especies que crecen sobre un sitio contaminado con cobre, fue posible seleccionar plantas adaptadas a ambientes semiáridos y adecuadas para ser utilizadas en programas de remediación de tranques de relaves.

Palabras clave: cobre, fitoextracción, fitoestabilización, remediación, plantas nativas.

INTRODUCTION

Copper is one of the most widely spread mineral resources on the earth's crust. In the north of Chile, soils are rich in metals, and copper is one of the most abundant components (Gonzalez et al. 1999). Chile has traditionally been dependent on copper exports; the state-owned company CODELCO is the world's largest copper-producing company, and foreign

private investment has developed many new mines. It has been estimated that copper production in Chile will grow approximately 30 % by the year 2012, contributing strongly to the country's economic development (Pérez 2006). However, copper extraction is an activity that has environmental impacts generated by the accumulation of wastes. The wastes are deposited in mine tailings made of fine particles generated after the extraction process. Mine tailings that are found in arid and semiarid regions where evaporation is high cause pollution by wind erosion, and the dust blown from the tailings has a high metal and metalloid content. If the mine wastes are not properly disposed of, there is a risk of spillage, seepage or landslides. Furthermore, the mine tailings and excavations have visual impacts on the environment (Miller 1999). A survey carried out by the Servicio Nacional de Geología y Minería (National Geology and Mining Service) (Sernageomin), recorded that more than 50 % of 665 mine tailings in Chile have no recovery plans and are subsequently abandoned (Sernageomin 2003). At present a specific regulation for abandoned mine sites is being discussed by the Chilean government, but no laws for recovering abandoned mine sites or to regulate the stability of the tailings have been approved.

During the last decade, phytoremediation, a technology that uses plants to remove, stabilize, or detoxify pollutants, has provided an effective and *in situ* alternative method to remediate contaminated soils (Baker et al. 1994[1], Blaylock 1997[2]). Under field conditions, there are several successful experiments in the phytostabilization metal-contaminated soils (Berti & Cunningham 2000). It is reported that phytoremediation not only reduces the environmental risk of soil metal contamination, but also increases the activity and diversity of

soil micro organisms and improves soil quality (Giller et al. 1998, Filip 2002). Successful phytoremediation depends on several factors; one of them is choosing the appropriate plant species that will be used in the remediation process (Marmiroli & McCutcheon 2003). This selection should be supported by the knowledge of metal-tolerant plant species capable of growing on toxic soils, and adapted to saline and normally acid substrates (Ginocchio & Baker 2004). Plants have the capability to rapidly adapt to their environment and evolve specific metal tolerance (Al-Hiyaly et al. 1990). In fact, most of the identified species that accumulate lead, cadmium, chromium, nickel, cobalt, copper, zinc, and selenium grow in sites with high metal content (Reeves & Baker 2000). Therefore, it is worthwhile to evaluate the potential for phytoremediation of plants that normally grow in sites with high metal content in order to make a primary selection of those that are suitable for tailings reclamation purposes.

Planta Matta is a copper processing plant located in the Third Region of Chile. It belongs to ENAMI, where flotation wastes have been accumulating for more than 20 years. The wastes have generated two tailings deposits that cover an area of approximately 1,000 m^2 to a height of 3 m with copper contents greater than 0.02 % (ENAMI 2005). A tree planting plan on one of the tailings deposits was undertaken in 1988 in order to stabilize the surface and reduce wind erosion. The first stage of the planting plan was implemented on a 250 m^2 area with six tree species: *Acacia cyanophyla*, *Schinus polygamus*, *Casuarina equisetifolia*, *Acacia melanoxylon*, *Cupressus macrocarpa*, and *Prosopis chilensis*. Young plants were planted using a random block design repeated three times. All the species used for the test were represented at least once in every block. The species were planted in a 30 x 30 x 30 cm grid at a distance of 2 m from one another. No additional materials were incorporated to the substrate, other than the soils in which the plants had been germinated and grown in the greenhouse.

In this study, we evaluate the results of the experiment with the following objectives: (1) to report plant species that survived and grew at the site; (2) to chemically characterize the soil of the tailings in vegetated and no vegetated

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[1]   BAKER AJM, SP MCGRATH, CMD SIDOLI & RD REEVES (1994) The possibility of in situ heavy metal decontamination of polluted soils using crops of metal-accumulating plants. Environmental Biotechnology in Waste Treatment & Recycle International Conference, Hong Kong. Resource Conservation Recycle 11: 41-49.

[2]   BLAYLOCK MJ (1997) Phytoremediation of lead contaminated soil at a brownfield site in New Jersey - A cost effective alternative. IBC's Second Annual Conference on Phytoremediation, June 18-19, 1997, Seattle, Washington, USA.

sectors; and (3) to determine copper concentration in the roots and leaves of plants growing in copper-polluted soils. We also discuss the appropriateness of using plant species to vegetate copper-polluted sites in an arid environment, and the potential for copper phytoextraction and phytostabilisation of plant species that grow in a copper-polluted site.

MATERIAL AND METHODS

Study site

The Planta Matta copper processing plant is located in the Third Region of Chile (27.3° S, 70.3° W), which has a desert climate with average temperatures of 19 °C in spring-summer and 14 °C in autumn-winter. Average annual rainfall is 20 mm, all of it in winter (Inzunza 2004). Average wind speed in spring-summer varies between 3.0 and 4.0 m s^{-1}, and wind direction has a westerly (W) component. In autumn-winter the average wind velocity varies between 2.0 and 3.0 m s^{-1}, and wind direction is SW to SE. The processing plant is 1

km from the Paipote Copper Refinery and 8.0 km from the city of Copiapó (Fig. 1).

Substrate analyses

Substrate samples were collected where plants were growing (vegetated substrate) and from no vegetated sectors (no vegetated substrate). Also, control soil samples were taken from a no polluted and no vegetated site 1 km from the tailings deposit. Sampling of the vegetated substrate was randomized using grids were each plant was numbered. Substrate samples were collected every three plants over an area of approximately 50 m^2. No vegetated substrate samples were taken from the same site in patches where no plants were growing. All the samples were taken from top to bottom at depth of 0-10 cm and 10-20 cm (fresh weight of approximately 1.5 kg). Roughly 20 g of samples were oven-dried overnight at 40 °C, homogenized, and sifted to a particle size of < 2.3 mm. Plant residues were carefully removed and the samples were analyzed according to standardized methods used at the certified analysis laboratory of the Instituto de
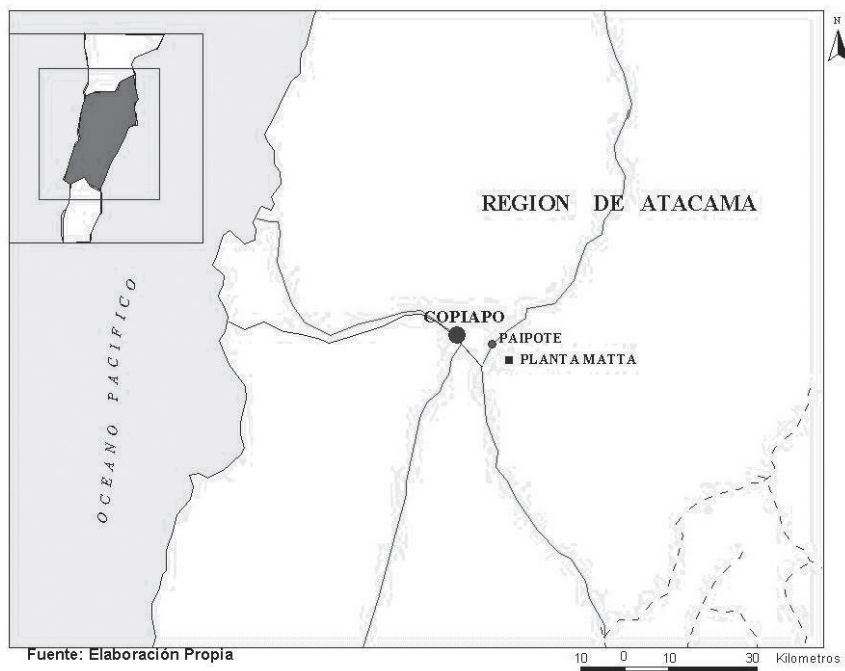
Fig 1: Map showing the location of the Planta Matta tailings deposit. The city of Copiapó is indicated.

Mapa de la ubicación del tranque de relaves de Planta Matta. Se indica la ciudad de Copiapó.

Investigación Científica y Tecnológica of the Universidad de Atacama (IDICTEC). To determine total metal concentration, 1 g of sifted sample was digested in a microwave oven (Milestone, model Mega 1200), with HNO_3 (70 %) and HF (40 %). After the digestion, the samples were cooled down, buffered with H_3BO_3, and filtered for further analysis (USEPA 1996). The concentrations of copper, arsenic, silver, lead and zinc were determined by flame atomic absorption spectrometry (AAS) (Perkin Elmer 3110 with FIAS-400 MHS-20 system). Mercury was determined using flow injection cold vapor generation coupled to AAS system (Boylan et al. 2001). The sample was dried and then thermally and chemically decomposed. The decomposition products were completely oxidized and the remaining decomposition products were carried to an amalgamator that selectively trapped mercury. After any remaining decomposition products were removed by oxygen, the amalgamator was rapidly heated, releasing mercury vapors. An oxygen flow carried the mercury vapors through absorbance cells positioned in the light path of the atomic absorption spectrophotometer (AAS). Total sulfur was determined by $BaCl_2$ precipitation. The pH was measured in a 1:2.5 (w w^{-1}) sample to deionized water mixture. Organic matter content was determined by the loss-on-ignition (LOI) method. A known weight of sample was placed in a ceramic container and heated at 440 °C overnight (ASTM, 2000). The sample's mass difference using the formula OM (%) = [(a-b)/(a-c)] x 100, where, a = dry sample (g) + container (g); b = burnt residue (g) + container (g); c = container (g). All weights were corrected for water content prior to the organic matter content calculation. Water content was measured as the ratio of the weight of water to the weight of the solids in a weighed mass of sample. The ratio was expressed as percentage of water. Extractable P was determined by the Olsen method, based on alkaline extraction by 0.5 N $NaHCO_3$ (Olsen & Sommers, 1982). Total reduced N was determined by the wet oxidation of soil using a micro Kjeldahl procedure with H_2SO_4 and digestion catalyst. Equilibrium extraction of exchangeable K was performed using 1 N CH_3COO (NH_4) (pH 7.0) and subsequent determination by AAS (Perkin Elmer 3110).

Plant analyses

Samples of nine plant species found in the 250 m^2 vegetated part of the tailings were collected. Some of the species collected were grasses that had colonized the site spontaneously. Five samples of each species were selected at random using grids at the sampling plot, where each plant was numbered. The individuals were collected every three numbered plants in the sampling plot over an area of approximately 50 m^2. Plant samples were collected by digging out the root system as completely as possible, thereby collecting the whole plants, which were immediately transported to the laboratory and were weighed (fresh weight) and divided for analysis into roots and leaves. Both fractions were washed with a solution of phosphate-free detergent, then with dilute HNO_3 solution (aqua regia), and finally with abundant deionized water. The samples were dried at 70 °C and ground to pass through a 500 μm stainless steel sieve. The material was then crushed and a 1.0-g representative sample was digested in 65 % HNO_3 and 35 % H_2O_2 for 15 min using a Milestone ETHOS D microwave system. The samples were placed in suitably microwave-inert polymer vessels that were sealed and heated in the microwave system. The temperature profile was 180 °C for 2 min, 200 °C for 11 min, and 210 °C for 5 min. After cooling, the vessels' contents were filtered through 0.2 μm membranes (Schleicher & Schuell MicroScience), and then analyzed for total copper content using AAS (Perkin Elmer 3110 with FIAS-400 MHS-20 system). A standard reference material with a certified copper content of 439 ± 22 mg kg^{-1} was used (TORT-1, National Research Council of Canada; lobster hepatopancreas; kindly provided by Universidad de Talca).

Statistical methods

Analysis of variance (ANOVA) was used for testing the copper content differences in the substrates and plant tissues. A significance level of $P < 0.05$ was used for the study. We used the Tukey honest significant difference as the posteriori test (α = 0.05). Statistical analyses were performed with Analyse-it Statistical Software (Analyse-it for Microsoft Excel, Leeds, United Kingdom: http://www.analyse-it.com/)

RESULTS

Substrate analyses

The substrate at the vegetated site had a neutral pH, low organic matter content, and high sulfur content (Table 1). The physicochemical parameters of the vegetated plots showed no significant differences in organic matter content and pH between the analyzed samples (vegetated, non-vegetated, and control) (Table 1). On the contrary, water content was significantly higher in samples where plants grew, compared to control soil. Both conductivity and salinity of the samples taken from the vegetated plot were lower than in the control soil. The non-vegetated substrate was composed of fine particulate matter and had a neutral pH, low organic matter content, and a high level of metals; mainly copper (Table 2).

When metal content in substrate samples was analyzed, we found that the copper, arsenic, and zinc content in the vegetated plot were significantly different for samples taken at different depths (Table 2). The metal content where most of the root tissue was found (0-10 cm depth) was similar to the amounts found in the control soil (Table 2). Total Fe content showed significantly higher values in the vegetated samples compared to the control soil, but Fe concentration was similar in the vegetated and no vegetated samples taken from the tailing deposit (Table 2). Phosphorus content (mg kg^{-1}) of the vegetated substrate at a depth of 0-10 cm was higher (5 ± 0.6 mg kg^{-1}) than at a depth of 10-20 cm (< 4). Nitrogen content neat the surface (0-10 cm) in the vegetated site was 124 ± 5.5 mg kg^{-1}, higher than the content found at 10-20 cm (70 ± 6.1 mg kg^{-1}). Non-significant differences were

TABLE 1

Physicochemical characterization of the vegetated substrate. Samples were taken at depths of 0-10 cm and 10-20 cm

Caracterización fisicoquímica del sustrato vegetado. Las muestras se tomaron a una profundidad de 0-10 cm., y 10-20 cm

Substrates	Organic matter(%)	pH	Conductivity (mS cm^{-1})	Salinity(mg L^{-1})	Total S(%)	Moisture(%)
Vegetated tailings(0-10 cm)	5.2 ± 1.1	7.4	1.9 [a]	1241 [a]	0.6 [a]	10.3 [a]
Vegetated tailings(10-20 cm)	4.7 ± 0.8	7.5	1.4 [a]	889 [b]	1.0 [b]	10.5 [a]
Non-vegetated tailings	5.1 ± 0.8	7.4	N.D.	N.D.	N.D.	N.D.
Controlsoil	5.9 ± 1.3	7.4	5.7 [b]	3622 [c]	0.6 [a]	2.3 [b]

Different letters represent differences between the samples; ND = not determined; mean ± SE for five samples are shown

TABLE 2

Total elements content of substrate samples taken from the studied site. Control samples were taken at a depth of 20 cm

Contenido total de elementos en muestras de sustrato no vegetado y suelo control. Las muestras control fueron tomadas a 20 cm. de profundidad

Element(mg kg^{-1})	Sample type			
	Control soil	No vegetated substrate	Vegetated substrat (0-10 cm depth)	Vegetated substrate (10-20 cm depth)
Cu	70 ± 1.8[a]	2550 ± 50 [b]	60 ± 3.1 [a]	290 ± 3.8 [c]
Zn	131 ± 9.1 [a]	210 ± 78 [a]	116 ± 3.2 [a]	216 ± 5 [a]
K	46 ± 1.5 [a]	55 ± 9 [a]	25 ± 2.1 [b]	21 ± 0.8 [b]
As	70 ± 5.4 [a]	75 ± 7.2 [a]	74 ± 2.2 [a]	136 ± 3.5 [b]
Fe	0.036 [a]	1244 ± 20 [b]	0.174 [c]	0.123 [c]

Different letters represent differences between samples; means ± SE for five samples are shown

found for the nitrogen content at the control site (182 ± 6.6 mg kg^{-1}). In the samples taken from the vegetated sectors of the tailings deposit at a depth of 0-10 cm and 10-20 cm there were significant differences in N, P, salinity, S, Cu, As, and Zn levels depending on the depth from which the samples were taken (Table 1 and Table 2). Contents of Hg, Ag, Pb and Se were also determined in the no vegetated site. Hg content was 0.5 mg kg^{-1}, Ag content was 2.4 ± 0.3 mg kg^{-1}, Pb content was 34 ± 2.7 mg kg^{-1}, and Se was 6 ± 1.3 mg kg^{-1}.

Copper content in plants

Nine vascular plant species were recorded in an area of 250 m^2. Five of the species were identified as native: *Baccharis salicifolia, Schinus polygamus, Atriplex deserticola, Scirpus asper,* and *Polypogon australis;* and four were identified as non-native species: *Casuarina equisetifolia, Acacia melanoxylon, Pennisetum clandestinum,* and *Cynodon dactylon.* Young and adult plants of the nine species were present, of which four grasses were found under the tree canopy. *Atriplex deserticola* plants were found on the slope of the tailings deposit.

Since copper was the most abundant metal present at the site, the level of this element was determined in 1.0 to 2.0 g (fresh weight) of leaves and roots of the nine species mentioned (Table 3). Copper accumulated both in the leaves and the roots of all the species in a species-dependent way. The amount of copper in leaves and roots in mg kg^{-1} of dry plant weight was used to calculate a leaves: roots (L:R) copper ratio. Copper content in stems was not determined. The L: R ratio ranged between 0.2 (*C. equisetifolia)* to 9.4 (*B. salicifolia).* Five species (*S. polygamus, B. salicifolia, S. asper, C. dactylon,* and *P. australis)* showed an L: R > 1.0, indicating copper movement from roots to shoots. *Casuarina equisetifolia, A. melanoxylon, A. deserticola,* and *P. clandestinum* had an L: R < 1.0, accumulating more copper in the roots than in the leaves (Table 3).

Three of the species found at the study site belonged to the *Poaceae* family (Table 3). *S. polygamus* and *A. deserticola* accumulated more than 1000 mg kg^{-1} of copper in their leaves. *A. deserticola* was particularly interesting because the plants found grew on the slope of the tailings deposit and had an abundant foliar mass. *Casuarina equisetifolia, A. deserticola, A. melanoxylon,* and *P. clandestinum* accumulated 1.6 to 6.0 times more copper in the roots than in the leaves (Table 3). In the present study the largest amount of root copper concentration was found in *C. equisetifolia,* which accumulated 2.9 g of Cu per kg dry weight.

The amount of copper found in the leaves of all the species was higher than 100 mg kg^{-1} of dry matter. A more detailed analysis indicated

TABLE 3

Copper content in leaves and roots of plants collected from the tailings deposit

Contenido de cobre en hojas y raíces de plantas colectadas en el tranque de relaves

Plant species	Copper content (mg kg^{-1} dry wt)		Leaves + roots copper (mg kg^{-1} dry wt)	Leaves:roots ratio(L:R)
	Leaves	Roots		
Baccharis salicifolia (PWS, As)	667.9 ± 2.4	71.3 ± 0.4	739.2	9.4
Schinus polygamus (P, Ana)	$1,213.5 \pm 8.9$	260 ± 0.9	1,473.5	4.7
Casuarina equisetifolia (P, Ca)	470.2 ± 3.3	$2,923.3 \pm 7.7$	3,393.5	0.2
Atriplex deserticota (PWS, Che)	$1,357.7 \pm 3.5$	2160 ± 71	3,517.7	0.6
Acacia melanoxylon (P, Le)	158.6 ± 1.6	484.0 ± 8.9	642.6	0.3
Pennisetum clandestinum (G, Po)	259.2 ± 6.2	866.4 ± 7.1	1,125.6	0.3
Scirpus asper (G, Cy)	459.3 ± 5.0	250.7 ± 6.1	710	1.8
Cynodon dactylon (G, Po)	246.5 ± 8.1	81.4 ± 0.6	327.9	3.0
Polypogon australis (G, Po)	669.5 ± 5.9	223 ± 16	892.5	3.0

P: perennial; PWS: persistent woody shoots; G: grass; Po: *Poaceae*; As: *Asteraceae*; Cy: *Cyperaceae*; Che: *Chenopodiaceae*; Ca: *Casuarinaceae*; Le: *Leguminosaceae*; Ana: *Anacardiaceae*; means ± SE for five samples are shown

that the largest copper content was found in the leaves of *S. polygamus* and *A. deserticola*, and the highest shoots-to-roots copper ratio, 9.4, was found in *B. salicifolia*. The grasses with the highest L:R ratio, between 1.8 and 3.0, were S. *asper*, *C. dactylon* and *P. australis* (Table 3), suggesting a movement of copper from roots to leaves in the plants. On the contrary, *P clandestinum* presented a shoots to roots ratio of less than 1.0, indicating more copper accumulation in the roots than in the leaves.

DISCUSSION

Although a substrate derived from a mine-tailing is not considered a proper type of soil, zinc and iron content in the samples were similar to those reported for serpentine soils (Reeves & Baker 2000). However, copper levels were much higher than expected for that type of soil, and potassium levels were about ten times lower than those reported for serpentine soils (Reeves & Baker 2000). On the other hand, arsenic content was similar to that reported by Bleymard & Bleiberg for lead/zinc type soils, except for the low lead level (Reeves & Baker 2000). Copper level in the samples was about 10 to 100 times higher than that found in soils used for agricultural purposes (Ginnocchio & Narvaez 2002). However, the copper level in the polluted site was lower than that n found in soils used for metal extraction or in tailings deposits (Reeves & Baker 2000). It might be possible that the presence of the plants had an effect on the availability of copper in the analyzed samples (Romkens et al. 1999).

The similar organic matter content in the three soil types analyzed may be due to a poor decomposition process and a low development of microbiota at the rhizosphere of the plants in the vegetated plot (Basta et al. 2005, Carrasco et al. 2006). The differences found in water content, conductivity, and salinity between the tailing area and the control area, where there has been no mining activity, may be due to the scarce vegetation found at the control site where the samples were taken, and the natural salinity of the soils in northern Chile (Celis & Letelier 1999). Under the arid conditions of the area where the control sampling was done there is little vegetation compared to the higher plant density at the tailings site. Plant roots in the polluted site have root matrices that contribute to maintain the substrate with more moisture that in the control site, because of the hydraulic effect of the roots of woody species. The root matrix in the tailings area would make less available the salts at the site, affecting the conductivity of the substrate (Angers & Caron 1998).

The bioavailability and solubility of metals in soils strongly depends on pH, organic matter, and the type and quantity of minerals (Delgado & Serey 2002). It has been shown that pH values below 5.5 may enhance Cu mobility, biological availability, and toxicity in soils (Martinez & Motto 2000), while organic matter "traps" the metal, lowering its bioavailability (Römkens et al. 1999). Sulfur content found at the vegetated site might be related to soluble copper/sulfur complexes of the ore from which copper was extracted, which are commonly found in tailings (Allen & Sheppard 1971, Macnair 1993). Although metal solubility in soil is a process that depends on several factors, as has been reported for Chilean soils by Ginocchio & Narvaez (2002), at the studied site it may be possible that the low organic matter content and the soluble form of copper are more important factors than the pH of the soil samples for the mobility of the metal from the substrate matrix to the plants. However, chemical analyses need to be performed to demonstrate this observation. The high copper levels found in the tissues of plant species growing at the site was an indication of the metal's mobility, and the distribution of Cu in plant tissues was an indication that the uptake by plants was a process depending on the biochemical mechanisms of each species (Song et al. 2004).

Individuals of *A. cyanophilla*, *C. macrocarpa* and *P. chilensis* that were originally planted at the site were not found at the time of the study. It is believed that the level of copper in the soil was too high and/or the plants were exposed for a long enough period of time to the metal, so the protection mechanisms were overwhelmed and the plants died after a few years (Ginocchio 2000). However, *A. melanoxylon*, *C. equisetifolia* and *S. polygamus* were still growing on the tailings, and some grass species had spontaneously

colonized the site. It may be that the surviving species developed copper tolerance through cellular mechanisms already described in the literature but not studied in this work (Pollard at al. 2002). The plant strategies to cope with the copper present in the polluted site could be either to exclude the metal at the root or to take the element up and partition it among the leaves, stem, and roots, or a combination of both (Baker 1981, Pollard et al. 2002).

Although copper is essential for plant growth, when present in large amounts in soils it is generally phytotoxic and can cause the death of the plants (Rhoads et al. 1989). Numerical thresholds for the metal in soil above which phytotoxicity occurs have been suggested, ranging from 140 to 280 mg kg^{-1} of total copper (Neuman et al. 1987). For most crop species, the critical level for copper toxicity in leaves is above 20 to 30 mg kg^{-1} dry wt. (McBride & Martinez 2000). Plants growing in soils with high metal concentrations due to human activities such as mining and smelting, behave as edaphic endemics (Kruckeberg & Rabinowitz 1985, Kruckeberg 1986) or pseudometallophytes, which are species that have populations on both metalliferous and nonmetalliferous soils (Bert et al. 2000). This is in agreement with several studies showing that metal tolerance is an adaptive physiological trait that can produce local ecotypes on metal-polluted soils (Bush & Barret 1993, Macnair et al. 1993). Plant species belonging to the *Asteraceae*, *Cyperaceae* and *Poaceae* families found at the polluted site (Table 3) showed copper content in leaves between 250 to 660 mg kg^{-1}, which is 5.0 to 12.0 times lower than the amounts reported for copper hyperaccumulator species of the same families (Reeves & Baker 2000). *Schinus polygamus* (*Anacardiaceae*) and *A. deserticola* (*Chenopodiaceae*) accumulated more than 1,000 mg kg^{-1} of copper in their leaves, so they might be considered as hyperaccumulator metallophytes according to the definition given by Malaise et al. (1978).

The amount of copper accumulated in the roots of *C. equisetifolia, A. deserticola, A. melanoxylon*, and *P. clandestinum* indicated that the four species have an extraordinary ability to take up copper from the polluted soils and to accumulate the metal in their roots, so they could be used to phytostabilize metal-polluted soils. In the present study the highest amount of copper in roots was found in *C. equisetifolia*, which accumulated 2.9 g kg^{-1} Cu, almost twice the amount of t metal found in tolerant copper-accumulators (Jiang et al. 2004). This result might be related to the spreading, fibrous root system that the plant can develop in a short time, so it can penetrate quite deeply into the soil, favoring uptake of the element (Torrey & Berg 1988).

The L: R ratios above 1.0 found in some of the species indicate a movement of the metal from the roots to the shoots, resulting in an accumulation of copper in the leaves, and a potential to extract copper from the site. This is particularly interesting for *S. polygamus, A. deserticola*, and *B. salicifolia* because the three species have been reported as deep-root plants adapted to arid environments (Gutiérrez et al. 2000). The ability of some plants to survive and reproduce while accumulating high concentrations of metals is a requirement when plants are used to immobilize metals present in polluted soils (Cai & Ma 2003). The toxicity of metals that are to be removed by the plants is a limiting step for the use of phytotechnologies, as is the stress caused by environmental conditions in the north of Chile, where several tailings deposits are located. Plant species which are able to grow and reproduce under these harsh conditions are of particular interest to phytotechnologies.

Although the grasses S. *asper*, *C*. *dactylon* and *P*. *australis* do not have deep root systems, the movement of copper to the aerial part of the plants as deduced by the S:R ratio found for them, makes them suitable for phytoextraction of the metal. Besides, the three species have a fast growth rate (Daehler 2003), so they can be harvested after a season of accumulation as has been suggested for *C. dactylon* (Madejon et al. 2002). However, the productivity of the species needs to be determined under field conditions to claim the proper use of the plants for phytoextraction purposes. The L: R ratio found for *P clandestinum* indicated copper accumulation in the roots and a potential for phytostabilization of copper-polluted sites.

Although copper content at the working plots was homogeneous (Table 2), the accumulation and tissue distribution of copper showed by the nine species screened was different and species-specific. It has been

shown that even when there are common mechanisms to tolerate metals in plants, the uptake and tolerance threshold are dependent on the plant's genetics (Macnair 1979, Rajakaruna 2004). Although the mechanisms involved in the plant uptake of copper were not studied in this work, the high levels of the metal found in the leaves and roots of the studied plants might be the result of a slow translocation caused by constant exposure to the copper present in the soils (Salgado & Serey 2002).

All the species showed desirable traits to phytoextract and/or phytostabilize copper-polluted soils, although only *S. polygamus* and *A. deserticola* can be considered as a pseudometallophytes for copper. If this condition has developed in these plants in the span of about 18 years, further investigation should be done, since it is generally believed that this process takes a much longer time than this. The endemic *A. deserticola* is adapted to the environmental conditions of the site, so the plants could grow and propagate easily. In a mine waste area located in an arid environment, phytostabilization of the tailings is more suitable than phytoextraction of the contaminant, due to the fact that cooper is present in high concentration and it is important to avoid the dispersion of contaminated dust. Phytoextraction is not efficient in an area where there is a large amount of contaminants (a too long time might be needed to "clean" the area), and there is always a risk of introducing copper into the food chain, if accumulator plants are consumed by animals. Taking this into account is very interesting to find autochthonous plants for stabilizing tailings due to the hard environmental conditions of Chile's northern regions. The pseudometallophyte species described could be very useful in cooper contaminated areas, yielding positive results in a cost/benefit analysis of this remedial action. We suggest using *S. polygamus* and *A. deserticola* for remediation of contaminated sites in arid and semi-arid regions of Chile. The two species are medium- to fast-growing plants which would favor soil stabilization. The use of a multispecific phytoremediation system has been recommended as an effective approach to clean and stabilize metal-polluted sites (Norman & Raforth 1998, Lambert et al. 1999).

A variety of root systems provided by different plant species would stabilize the soil mimicking wind erosion and material slides, typically occurring in arid and semiarid regions (Smith at al. 1998, Baer et al. 2005).

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