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Changes in the sorption, desorption, distribution, and availability of copper, induced by application of sewage sludge on Chilean soils contaminated by mine tailings

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Abstract

The effect of mine tailings and sewage sludge was evaluated on sorption, desorption, availability and distribution of copper in two soils, one high (sandy soil) and one low in copper (clay soil). In both soils contaminated by mine tailings the copper sorption capacity and the affinity of the substrate for the metal decreased substantially compared to the uncontaminated soils, however, the sorption remained always high in the clay soil substrates. In the substrates with sandy soil, the high Cu content and lower clay content were determining factors in the lower magnitude of the sorption. Similarly, metal desorption was closely related to these two parameters, and it was higher in clay soil with lower pH. In general, the application of sewage sludge favored the sorption of Cu in soils contaminated and uncontaminated with mine tailings, and in all cases desorption decreased, an effect that remained for at least 30 days. Simple extraction of Cu with $CaCl_2$ and diethylenetriaminepentaacetic acid gave contradictory results, so a careful choice of the procedure is required, depending on the level of metal in the soil and on the acting principle of the extracting agent. In that relation, more complete information on the changes in the metal forms was obtained by application of the sequential extraction procedure proposed by the European Community Bureau of Reference.

Key words: sewage sludge; copper sorption; mine tailings; copper desorption; European Community Bureau of Reference; sequential extraction

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Introduction

Contamination of soil and water with copper (Cu) is a ubiquitous environmental problem that is associated with diverse human activities such as ore smelting processes, metallurgy, application of biocides containing Cu in agriculture, and mostly Cu mining activities.

Copper mining produces large volumes of solid and liquid wastes that generally involve impoundments designed to accumulate wastes for several decades (Kelm et al., 2009). As mining activity increases, new impoundments are built further away from the mining complex, and that implies the construction of ducts for transporting the mine tailings through vast agricultural zones. This environmental scenario involves a permanent risk of accidental spills of residues, leading to the contamination of agricultural soils near the waste deposits or the ducts that transport mine tailings. There have been reports of several accidental tailings spills that have affected the plants and animals around the sites and have rendered useless large areas of agricultural soils (Aguilar et al., 2004; Rodríguez et al., 2009).

One of the strategies used to recover soils contaminated with mine tailings is the *in situ* application of materials that ideally increase metal retention in the soil and favor the reestablishment of the vegetable layer (Kumpiene et al., 2008; Moreno-Jiménez et al., 2011; Zhang et al., 2011). In that sense, the application of organic amendments in various laboratory and field experiments has been shown to be effective for the recovery of contaminated soils (Guo et al., 2006; Nwachukwu and Pulford, 2008). Some of the advantages of these materials include, in general, their high organic matter content, high buffering capacity that allows adjusting the pH of the soil, good contribution of nutrients for the development of plants, and in most cases they are low cost materials (Guo et al., 2006).

The application of sewage sludge (SS) to soil as a way of making them available is a habitual practice in many countries (Epstein, 2003). Although their application to soils contaminated with mine tailings is relatively recent, various studies report beneficial effects that result in greater retention of metals owing to the contribution of new sites for sorption (Pond et al., 2005), decreased phytoavailability (Khan and Jones, 2008; Santibáñez et al., 2008), or improvement of the conditions for the establishment of

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vegetation (Gardner et al., 2010; He et al., 2007).

Evaluation of the effectiveness of the amendments is even more necessary when dealing with soils contaminated with mine tailings, because the effectiveness can vary depending on the composition of the mine tailings, which in turn depends on the type of mineral that gives rise to them, the physicochemical characteristics of the soil, its ability to retain metals, and the supply of nutrients by the amendment (Guo et al., 2006).

The Cu sorption and desorption processes in soil are fundamental for keeping the levels of availability and bioavailability of the metal. There are several factors that can alter the magnitude of these processes, such as the presence of contaminants and other metals, changes in the content and quality of organic matter, changes in pH, and cation exchange capacity (Rooney et al., 2006; Sparks, 2005). Sorption and desorption of Cu in a soil involves mainly the negatively charged surfaces of organic matter, clay, and metal oxides or hydroxides with which Cu can establish interactions that go from weak Van der Waals type interactions to stronger bonds involving the formation of inner sphere complexes (Sposito, 2008).

To evaluate the amount of Cu available to the plants, several one-step extraction methods have been proposed, because they are simpler and they facilitate the operation. Some of the most widely used extracting agents are diethylenetriaminepentaacetic acid (DTPA) and ethylene-diamine tetraacetic acid (EDTA) because of the ease with which they form stable Cu complexes. On the other hand, the neutral salts $CaCl_2$ and $NaNO_3$ have been used frequently because they are naturally present as electrolytes in the soil solution (Haq et al., 1980). Although they are more tedious procedures, the sequential extraction schemes of metals by the consecutive application of different chemical agents with greater extractive strength is another way of evaluating the changes produced in the forms of a metal in contaminated substrates (Rauret et al., 1999; Mendoza et al., 2006).

In the central valley of Chile intensive agriculture coexists with mining centers involved in the extraction of Cu and other elements. Several zones close to the mining centers present soils with high contents of total and available Cu (Ahumada et al., 2004; Mendoza et al., 2006; Montenegro et al., 2009) which should indicate varying levels of Cu contamination derived from mining activities.

This study considered the preparation of substrates consisting of mine wastes and soils close to the tailings impoundments, which were mixed to form substrates that simulate soil contamination due to accidental spilling of those wastes. These substrates were used to evaluate the changes produced by the application of SS from domestic sewage treatment and by the natural aging of the substrates treated with SS over a short period of time (30 days). Cu sorption and desorption were evaluated in the treated and incubated substrates in the eventuality of the substrates receiving liquid wastes with a high dissolved metal content. The changes in the extractability and distribution of the Cu forms produced by the SS were also evaluated to establish their effectiveness and applicability in episodes of contamination with mine tailings.

1 Materials and methods

1.1 Mine tailings, soil, and SS

The mine tailings were obtained from a mining center located in the sixth region of Chile where ores are extracted and processed to obtain Cu. These procedures take place in the high mountain and the residues are transported to tailings impoundments located in the valley. During several decades these sites have received the residues produced by the main mining center and at present, the gange deposited there is being reprocessed to recover mainly Cu and Mo. In many cases, the areas near the tailings impoundments are soils in which a variety of agricultural activities are carried out. Two soils from those areas were chosen, Cauquenes (CQ) and Requinoa (RQ), located 2 and 5 km away, respectively, from the tailings impoundments. On both soils there is intensive cultivation of cereals and vegetables. This study considered SS from sewage treatment plants consisting of wastes with high organic matter content whose main destination is sanitary landfills. The substrates were characterized using the method described by Blakemore et al. (1987).

The soils of 0–20 cm depth were air-dried and sieved through 2 mm screen. The mine tailings and SS were dried in an oven at 50°C for 48 hr and then ground and sieved through 2 mm screen.

1.2 Preparation of the substrates and incubation

The soils were mixed with the mine tailings in a 3:2 (W/W) soil:tailings ratio. The mixtures were shaken vigorously in polyethylene bags to ensure homogeneity of the particulate material. The SS was applied in an amount equivalent to 200 Mg/ha in each substrate amended. The content of each bag was distributed in four 1-L pots, adding water to reach its field capacity. The pots were kept slightly open in darkness for 30 days at (25±1)°C in an incubator, recovering the lost moisture periodically.

1.3 Sorption and desorption of copper

Before getting the sorption isotherm, the time needed for the process to reach equilibrium was determined through the sorption kinetics by applying to the substrates a 5 mmol/L $Cu(NO_3)_2$ solution at pH 5.0 in 0.1 mol/L KNO_3, in a 1:20 (W/V) amendment: solution ratio, stirring for 4, 8, 16, and 24 hr. The mixture was then centrifuged and the supernatant was filtered. The metal at equilibrium was measured in the solution by flame atomic absorption spectroscopy (FAAS) (3110, PerkinElmer, USA).

Copper sorption was carried out in batch experiments using 50-mL polyethylene centrifuge tubes and a 1:20 (W/V) substrate:liquid ratio. The Cu concentrations used were 0, 0.5, 1, 1.5, 2, 3, and 4 mmol/L at pH 5.0, prepared from a $CuNO_3$ stock solution; each applied solution also contained 0.1 mol/L KNO_3. From the estimated time for

the sorption kinetics, the suspension was stirred for 16 hr at $(20\pm1)°C$, recording their initial and final pH. Then the suspension was centrifuged, and the supernatant was filtered, and the metal in equilibrium was measured by FAAS. Each concentration point was prepared in duplicate. The amount of sorbed Cu was determined from the difference between the Cu concentrations in the original solution and in the solution at equilibrium, and was expressed in grams of Cu per kilogram of substrate. The data obtained for the ratio of Cu at equilibrium and sorbed Cu were analyzed statistically. Each data set was fitted to Langmuir isotherm model, using a nonlinear regression method.

For the desorption study the substrate was previously saturated with Cu by applying 8 mmol/L $Cu(NO_3)_2$ at pH 5.0 and stirring for 16 hr. The sorbed metal was calculated as described in the previous point. After removing the solution at equilibrium, desorption was carried out by applying a 0.1 mol/L KNO_3 solution at pH 5.0, which was replaced by fresh solution at 2, 4, 10 and 24 hr after the beginning of the desorption. The weight of the tubes with the solid phase was recorded at each stage of the process for the later correction of the data, subtracting the amount of metal in the liquid imbibed in the solid. The metal in the solution of each stage was determined by FAAS. Total desorbed Cu was calculated as the sum of the amounts desorbed in each stage.

1.4 Simple and sequential extraction, and determination of total Cu in substrates

The available Cu in the soil, treated and untreated, was estimated by means of two simple extraction procedures, namely 0.01 mol/L $CaCl_2$ (Houba et al., 1996) and DTPA (Lindsay and Norvell, 1978), while the metal forms were estimated by the sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) (Mendoza et al., 2006).

The sequential extraction procedure consisted of three stages. In the first step, the water-soluble and exchangeable fraction (HOAc-soluble fraction) was obtained. In the second step, the forms bound to manganese and iron oxides (reducible fraction) were obtained. In the third step, organically bound metals and sulfides were extracted (oxidizable fraction). Finally, the difference between the sum of the fractions mentioned above and the total metal was considered as metal occluded in the crystal structures of the primary and secondary minerals (residual fraction). Total metal in the soil was determined by FAAS, prior digestion of the samples in a 2:1:1 mixture of HNO_3:H_2O_2:HF (V/V/V) in a microwave oven (MLS1200, Milestone, Italy).

1.5 Statistical analysis

The data were subjected to one-way analysis of variance (ANOVA) using Statgraphics (v. 4.0) statistical package for Window. Where significant F-values were obtained, the individual means were compared by Duncan's test to a level of 5%. Statgraphics was also used to fit the sorption data with the model of Langmuir isotherm.

2 Results and discussion

2.1 Characteristics of the soils, mine tailing and SS

Table 1 shows the main physicochemical characteristics of the mine tailings, the soils and the amendment. The pH of water in both soils was close to neutral, but the pH in KCl, which reveals the potential acidity of a soil, indicates acidic soils. The difference between the pH in water and in KCl ($\Delta pH_{water-KCl}$) in both soils was about one pH unit, pointing to soils with low saturation of the sites by K^+, Mg^{2+} and Ca^{2+} ions. The conductivity of both soils was low, indicating a low content of dissolved salts. Organic matter was found in a range similar to that of agricultural soils in the central valley of Chile (Ahumada et al., 2004; Mendoza et al., 2006). The texture determined for the CQ and RQ soils was sandy loam and clay, respectively. In soil RQ the clay fraction was predominant, with 450 g/kg, in contrast with soil CQ, where it reached only 150 g/kg, with a predominant sand fraction of 650 g/kg.

Soil CQ had a much higher total Cu concentration compared to soil RQ, probably due to the constant exposure of that site to contamination from mining activity wastes through water or air, a fact that also agrees with the high level of available Cu present in this soil (260 mg/kg). Also, this site shows high levels of molybdenum, and in that respect there are few studies on the characteristics of the soils close to the mining center. In a recent study Kelm et al. (2009) reported on soils in the Machalí sector, next to soil CQ of this study, where they found < 100 mg/kg of Cu and Zn, < 10 mg/kg of As and Pb, and <1 mg/kg of Mo in superficial soil. On the other hand, soil

Table 1 Physical and chemical properties of soils, mine tailing (MT) and sewage sludge (SS)*

Analysis	CQ soil	RQ soil	MT	SS
pH (H_2O)	7.88	6.93	4.38	6.43
pH (KCl)	6.54	5.22	3.59	6.26
EC (dS/m)	0.92	1.71	5.21	1.72
Organic carbon (%)	1.3	3.5	nd	28
Organic matter (%)	2.20	6.02	–	–
CEC (cmol(+)/kg)	12.2	40	–	72
Texture	Sandy loam	Clay	–	–
Total metal				
Cd (mg/kg)	nd	nd	nd	3.2
Cr (mg/kg)	21 ± 0.9	12 ± 1	53 ± 0.4	24
Cu (mg/kg)	1970 ± 23	169 ± 3	1179 ±185	672
Mn (mg/kg)	944 ± 7	1126 ± 33	5.3 ±0.4	363
Mo (mg/kg)	74 ± 4	nd	267 ± 2	–
Ni (mg/kg)	19 ± 0.5	nd	19 ± 3	36
Pb (mg/kg)	nd	nd	nd	80
Zn (mg/kg)	198 ± 26	160 ± 16	51.1 ± 0.7	757
Al (g/kg)	29 ± 1	35 ± 3	–	–
Ca (g/kg)	8.0 ± 0.5	4.4 ± 0.4	–	42
Fe (g/kg)	54 ± 0.2	62 ± 0.4	–	25
Mg (g/kg)	0.4 ± 0.05	0.75 ± 0.04	0.55 ± 0.09	6.8
DTPA-extractable metal				
Cu (mg/kg)	260 ± 5	20 ± 0.3	–	–
Zn (mg/kg)	2.3 ± 0.1	1.8 ± 0.1	–	–
Mn (mg/kg)	7.2 ± 0.1	116 ± 1	–	–
Fe (mg/kg)	18 ± 0.4	141 ± 2	–	–

*Results determined in duplicate, mean ± standard deviation (n = 4).
nd: not detected; –: not determined.
EC: electrical conductivity; CEC: cation exchange capacity.

RQ is protected by a natural barrier of hills that would prevent transfer of contaminants in liquid percolate from the tailings impoundment, or of contaminated particulate matter dispersed by the wind from the mine tailings or the smelter. This would account for the lower Cu and Mo content of this soil. In both soils the other elements are present at the normal levels found in the soils of the central valley (Luzio et al., 2010).

With respect to the levels of available metal, in both soils Cu is more available than Zn, Mn and Fe. The available Cu levels represent around 13% of total Cu in both soils. Available Zn, Mn and Fe are lower than 1%, except Mn in soil RQ.

The mine tailings consist of sandy matter of fine granulometry, with moderately acid pH, a total Cu content higher than 1000 mg/kg but lower than the Cu content of soil CQ, and also high Mo content, low levels of other heavy metals, lack of organic carbon, high levels of sulfate, and low cation exchange capacity (CEC). The main components of the mine tailings are quartz, pyrite, hematite, K-feldspar, plagioclase, biotite, calcite, anhydrite, tourmaline, rutile, apatite, white mica, chlorite, epitope, kaolinite, and montmorillonite (Dold and Fontboté, 2001; Kelm et al., 2009).

The amendment chosen was a SS with high organic matter content, relatively abundant in areas close to the studied soils. The pH of the SS (Table 1) was in the slightly to moderately acid range. The metal content was found at levels usually described in SS from wastewater treatment plants, yet SS complies with the Chilean standard that governs the application of these wastes to agricultural soils (DS-004, 2009).

2.2 Sorption of Cu by the substrates consisting of soils, mine tailings, and SS

Previously, it was established that under the experimental conditions used for the sorption process, the time needed for the process to reach equilibrium was a minimum of 8 hours, keeping those conditions for at least 24 hr. For that reason a time of 16 hr was chosen for the sorption process in the SS as well as in the treated soils.

Figure 1 shows the sorption isotherms of Cu in soils CQ and RQ treated with mine tailings and SS. In all cases the shape of the isotherm corresponds to type H or L (Sposito, 2008), showing clearly a range of Cu concentrations at which there is saturation of the sorption sites and therefore maximum sorption of the metal. The goodness of fit of the data for the Langmuir model was good, with R^2 between 0.90 and 0.97 (Table 2). The Langmuir model calculates parameter b, which corresponds to the maximum Cu sorption capacity in the substrate. Thus, comparison of this parameter between treatments allowed us to estimate the changes produced by SS and mine tailings in the Cu sorption.

In both soils Cu sorption was always higher in the uncontaminated soil than in the soil contaminated with mine tailings. The application of SS to soil CQ treated and untreated with mine tailings increased the sorption by 120% and 60%, respectively. In the case of soil RQ these increases were 63% and 44%, respectively. Comparison of each treatment between both soils showed that soil RQ sorbed more Cu than soil CQ, with values of b between 1.2 and 2.1 units higher.
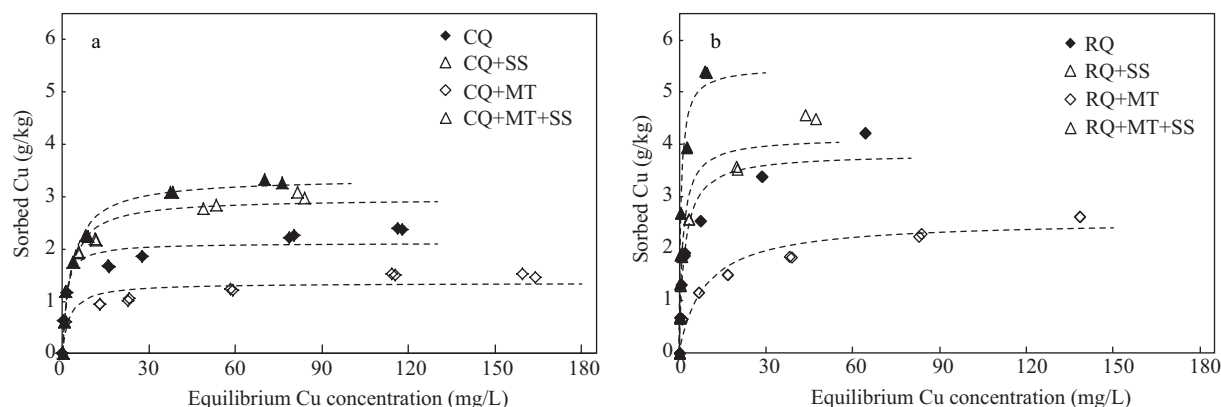
Fig. 1 Sorption isotherms of Cu on CQ soil (a) and RQ soil (b) ($n = 14$) treated with mine tailings (MT) and SS. Symbols represent experimental data and the dotted line represents the fit of data to the Langmuir model.

Table 2 Parameters of Langmuir model for Cu sorption, Cu desorption from substrates, difference between pH$_{water}$ and pH$_{KCl}$, and pH of substrates with sorbed Cu before starting desorption

	K (L/mg)	b	R^2	Desorbed Cu (%)	ΔpH$_{water-KCl}$	pH before starting desorption
CQ	0.838 ± 0.316	2.115 ± 0.109	0.90	10.5 c*	0.81	5.13
CQ+SS	0.305 ± 0.051	3.357 ± 0.144	0.96	9.8 b	0.36	4.95
CQ+MT	0.418 ± 0.164	1.351 ± 0.068	0.90	11.4 c	0.83	4.76
CQ+MT+SS	0.368 ± 0.066	2.965 ± 0.117	0.96	5.9 a	0.26	4.80
RQ	0.535 ± 0.128	3.826 ± 0.202	0.94	21.5 e	1.26	4.43
RQ+SS	1.583 ± 0.227	5.493 ± 0.251	0.97	9.6 b	0.67	5.16
RQ+MT	0.112 ± 0.028	2.539 ± 0.143	0.94	29.2 f	1.10	4.18
RQ+MT+SS	0.798 ± 0.158	4.139 ± 0.198	0.95	15.2 d	0.53	4.80

Parameters K and b are the mean value $\pm$ standard deviation ($n = 14$).
* Mean ($n = 3$), results followed by the same letter are not significantly different at $p < 0.05$.

On the other hand, the fit of the data with Langmuir model allowed the estimation of parameter K (Table 2), which represents the affinity of the sorbate for the adsorbent (Sposito, 2008). The affinity for Cu shown by the different substrates varied between 0.112 and 1.600 L/mg. Similar values have been described for Cu in soils (Mesquita and Vieira e Silva, 2002; Maftoun et al., 2002), and component fractions of soils (Farrah et al., 1980). Although K as an indicator of the affinity of a metal for the adsorbent is debatable (Sparks, 2005), the good fit of the data with Langmuir model achieved in this work allows inferring that the application of SS to soil CQ decreases affinity by 65%, but does not modify it in soil contaminated with mine tailings. In soil RQ the addition of SS increased the affinity for Cu by 200% and 600%, in soil untreated and treated with mine tailings, respectively.

2.3 Desorption of copper from substrates

Table 2 presents the results of desorbed Cu from the originally sorbed metal at 24 hr after starting the process. According to the information reported by Atanassova and Okazaki (1997), this amount corresponds to nonspecifically adsorbed Cu. In this study, the largest amount of desorbed metal was obtained during the initial few hours. Thereby, after 10 hr about 88% of the total desorbed metal had already been desorbed (data not shown). The substrates with soil CQ showed a lower range of variation (6%–11%) than the substrates with soil RQ (9–29%), with soil CQ showing a higher Cu retaining capacity.

In soils treated with mine tailings, the SS decrease desorption in a range of 5–14 percentage points, the effect being more noticeable in soil RQ. In untreated soils the application of SS to soil CQ practically did not change Cu retention, but in soil RQ desorption decreased substantially by about 12 percentage points.

For any of the treatments, desorption was greater in the substrates with soil RQ, a result that contrasts with the higher clay and organic matter content of this soil compared to soil CQ. Both clay and organic matter would contribute to increase the sorption of metals by strong or weak bonding with them (Sposito, 2008). However, a better explanation of the results of this study would be the lower pH presented in general by the substrates consisting of soil RQ (Table 2). In that sense, the pH of the original soil RQ (Table 1) and the pH achieved in the process of sorption for each treatment (Table 2) were lower than that of the substrates with soil CQ. Similarly, the substrates with RQ had a potential acidity ($\Delta pH_{water-KCl}$) greater than the substrates with soil CQ.

Related to the above, the clay content of soil RQ would also contribute to explain the results. In that sense it has already been stated that the Cu sorption process in the clay fraction separated from the soil has been found to be highly dependent on pH (Atanassova and Okasaki, 1997; Cavallaro and McBride, 1984), and this has been attributed to the sorption of hydrolyzed species of the metal ($CuOH^+$). On the other hand, Atanassova (1995) has shown that the clay fraction of the soils is the main adsorbent of Cu, and there is a positive correlation between

the content of Al-Fe oxy-hydroxides and the adsorption of Cu. In relation to this, Atanassova and Okasaki (1997) have shown that a considerable amount of sorbed Cu can be solubilized by decreasing pH to 4 in soils with high clay content. In the present study no detailed analysis was made of the clay fraction of both soils, but clearly soil RQ has high clay content (450 g/kg), a fact that associated with its lower pH, making it more susceptible to changes in the sorption and desorption of Cu due to pH changes. In this study, when the pH of the substrates with sorbed Cu was correlated with the desorbed metal fraction in soil RQ (Table 2), a good correlation was obtained between both variables ($r = -0.988$, $p < 0.05$); however, in soil CQ the two variables were not correlated.

2.4 Extractability of Cu from the substrates

The results for the simple extraction showed a clear differentiation between the amounts of Cu extracted with $CaCl_2$ and DTPA (Table 3). For $CaCl_2$ extraction, regardless of the treatment, 2.70 and 0.26 mg/kg on the average were extracted from soils CQ and RQ, respectively, amounts that represent a small fraction of the exchangeable Cu present in the soils that can be leached by a solution with a pH, composition, and concentration similar to that of a soil solution like 0.01 mol/L $CaCl_2$ (Houba et al., 1996). In DTPA extraction, regardless of the treatment, the complexing agent was able to extract an average of 218 and 33 mg/kg from soils CQ and RQ, respectively. This fraction may come mainly from exchangeable forms and in a lower proportion from metal linked to carbonate. The amount extracted by complexing agents is frequently associated with the amount of metal available to the plants, and these agents are widely used due to their ability to form well-defined, stable, and water soluble complexes with metal cations (Feng et al., 2005).

With respect to the effect of SS, in soil CQ this amendment did not modify the Cu extractable with DTPA, but in the same soil treated with mine tailings a 38% increase took place. In soil RQ the SS increased extractable Cu by 55%, and on the contrary, in soil with mine tailings the amendment caused a slight decrease of extractable Cu by an average of 4%.

In the eventual contamination of a soil with mine tailings, followed by the immediate application of SS and the natural aging of the resultant substrate for 30 days,

Table 3 Cu obtained by simple extraction with DTPA and $CaCl_2$, and HOAc-soluble form by the BCR sequential extraction

	Cu (mg/kg)		
	DTPA	$CaCl_2$	HOAc-soluble
CQ	270 g	0.58 b	598 g
CQ+SS	271 g	5.16 d	408 f
CQ+MT	139 e	0.40 a	396 e
CQ+MT+SS	192 f	4.57 c	264 d
RQ	21.6 a	nd	nd
RQ+SS	33.6 b	0.43 a	3.0 a
RQ+MT	39.5 d	nd	3.5 b
RQ+MT+SS	37.8 c	0.61 b	5.0 c

Data are presented as mean value ($n = 3$), data for each extractant followed by the same letter were not significantly different at $p < 0.05$.

the simple extraction of Cu generates contradictory results (Tables 1 and 3) that depend on the level of total Cu present in the substrates and on the agent used. In substrates with low or normal total Cu content, the SS tend to mobilize the metal, as seen in soil RQ by $CaCl_2$ (from not detected to 0.61 mg/kg) and by DTPA (from 20 to 37.8 mg/kg). On the contrary, in substrates with abnormally high Cu levels, after 30 days the SS decreases substantially the mobility of the metal when it is extracted with DTPA (from 260 to 192 mg/kg), but it increases it slightly when the Cu is extracted with $CaCl_2$. However, the discrete increased mobility of Cu observed in the substrates does not imply a phytotoxicity risk, since other studies (Moreno-Jiménez et al., 2011; Lu et al., 2009) have indicated the absence of deleterious effects of Cu to plants at those levels of available metal.

2.5 Sequential extraction

The distribution of copper among the various forms in the soil was different (Fig. 2). In soil CQ the order was soluble = reducible > oxidizable > residual, while in soil RQ the order was oxidizable > residual >> reducible > soluble. These results agree with the distribution found in soils with high Cu content of anthropic origin, in which in general there is a prevalence of more labile forms of the metal (Lu et al., 2009). Also, in the case of soil RQ its distribution agrees with that found in soils with naturally low Cu content, where less labile species prevail (Mendoza et al., 2006).

The application of SS to soil CQ decreased soluble Cu by approximately 7 percentage points and increased the oxidizable form by around 10 percentage points. This result can be accounted for by the high contribution of organic matter made by the SS, which would favor the bonding of the metal to the organic fraction. In soil RQ treatment with SS produced only slight changes in the distribution, with a more noticeable increase of soluble Cu.

Replacement of 40% of the soil by mine tailings caused various changes in the distribution of Cu in the soil-tailings resulting mixtures, which are explained by the lower total metal content and the higher proportion of the residual, oxidizable, and soluble forms present in the mine tailings. In soil CQ this caused a slight decrease of Cu forms linked with oxides and organic matter, and an increase of the residual form. In soil RQ it caused an increase of the

soluble, reducible, and residual forms, and a decrease of the oxidizable form.

The application of SS to soil CQ contaminated with mine tailings, as well as to soil without mine tailings, caused a substantial increase of Cu linked to the oxidizable fraction and a decrease of soluble Cu. In the case of soil RQ contaminated with mine tailings, the application of SS also increased the fraction bonded to organic matter, but this took place together with the decrease of the reducible and residual fractions and an increase of the soluble fraction.

Considering that the more labile forms of Cu have greater incidence on the toxic effect and the mobility of the metal, comparison of the amount of metal in the HOAc-soluble fraction obtained by the sequential extraction in the different treatments (Table 3) makes it possible to highlight the effect of the mine tailings and SS on the soil. In soil CQ the SS decreased substantially the Cu extractable with HOAc with an average decrease of 190 mg/kg. Under the same conditions, in soil treated with mine tailings the SS caused an average decrease of 132 mg/kg. Similarly, the combined application of SS and incubation for 30 days caused a decrease of HOAc-soluble Cu of 142 and 195 mg/kg in soil treated and untreated with mine tailings, respectively. In the case of soil RQ, this comparison indicated slight increases of 2 and 3 mg/kg, respectively.

3 Conclusions

In soils contaminated with mine tailings, the sorption capacity and affinity of the substrate for Cu decreased substantially compared to uncontaminated soil. That effect is probably due to the decrease of the bonding sites contributed by the soil and to the lower pH resulting from the soil-tailings mixture. On the other hand, the sewage sludge constitutes a good source of organic matter that contributes new sites for the sorption of metals, particularly Cu. These materials applied to soils contaminated with mine tailings improve Cu retention, an effect that remains for a period of at least 30 days of natural aging of the substrates.

Since the simple Cu extraction procedures yield contradictory results, it is necessary to make a careful selection of the procedure, depending on the level of metal in the soil and the acting principle of the extracting agent, in such a way that the simple extraction procedure reflects more accurately the changes in the amounts of the labile Cu fractions after contamination of the soil with mine tailings or after the application of SS. In that respect, more complete information on the changes undergone by the metal forms was obtained by the application of the BCR sequential extraction procedure.

The results of this study would support the application of sewage sludge on the soil immediately after the occurrence of the contamination event, but it is necessary to evaluate the impact of the application of large amounts of these amendments on the mobility of nutrients in the soil, the content of pathogens, and the leaching of metals and nutrients to subsuperficial soil layers.
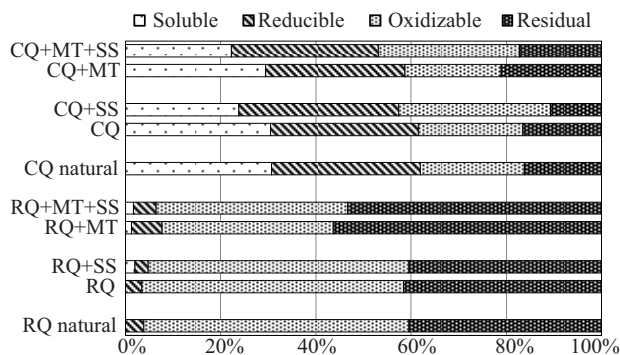

Fig. 2 Distribution of Cu obtained by sequential extraction in the substrates incubated for 30 days.

Acknowledgments

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