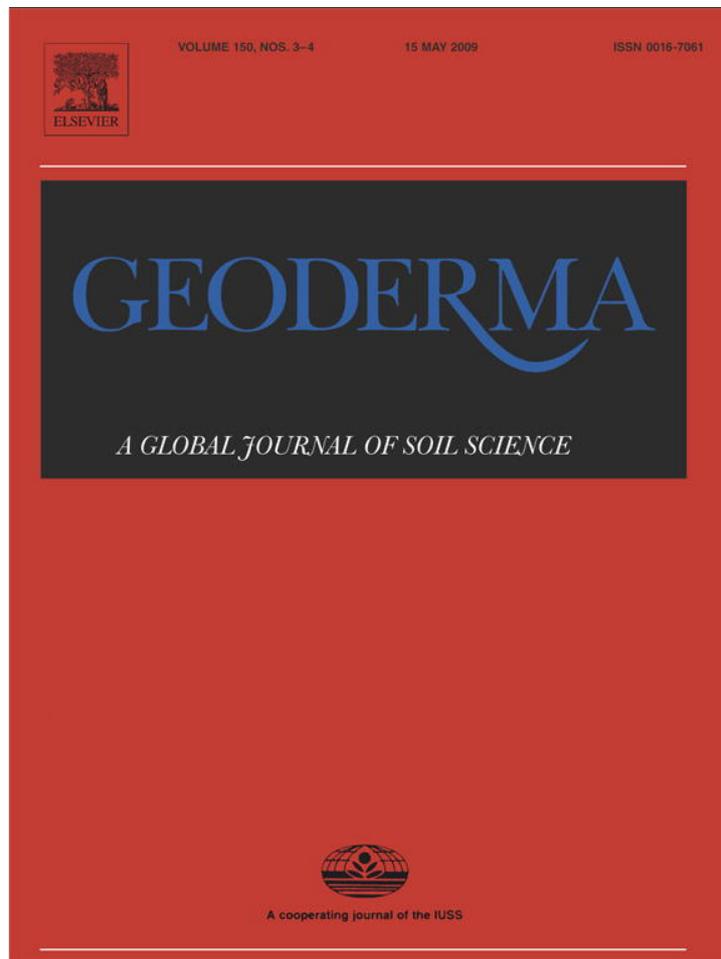


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Copper mobility in contaminated soils of the Puchuncaví valley, central Chile

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ABSTRACT

We studied soils exposed to emissions from the Ventanas copper smelter in central Chile. Values of pH, free Cu²⁺ activity, and total dissolved copper were determined in the saturated paste extracts and the soil solutions collected by means of perforated plastic bottles installed in situ. Soil solutions were collected based on the periodicity of the rain. The topsoils (up to 30 cm) exhibited pH values in the saturated paste extracts of 4.6–5.5 and total soil copper concentrations of 310–640 mg/kg. In contrast, subsoils exhibited pH values in the saturated paste extracts of 6.4–7.2 and total soil copper concentrations of 30–60 mg/kg. These data suggest that the anthropogenic inputs of the Ventanas smelter, with respect to increase in Cu concentrations and acidification, are restricted to the topsoil while the subsoil remains unaffected. The above observations are probably due to sandy loam texture of the topsoils that allowed rapid water infiltration that did not allow the equilibrium between the rain water and the soil constituents to be reached. Consistent with this argument, soil solutions were not as acid as saturated paste extracts. Likewise, free Cu²⁺ activities and total dissolved copper concentrations in the soil solutions were lower in the saturated paste extracts. Thus, saturated paste extracts were not a good proxy of soil solutions for short-duration and intense rain events. In situ soil solution sampling by simple and low-cost devices, such as perforated plastic bottles used in this study, is a better mean for assessment of metal mobility in contaminated soils than saturated paste extracts. In solutions percolating through the soil during rain events, dissolved organic carbon was the major factor controlling total dissolved copper concentrations while soil pH was the major factor controlling the free Cu²⁺ activity.

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1. Introduction

At metal-contaminated sites, there is a particular concern of whether metals are mobile in the soil profile (Vangronsveld et al., 1995). If metals are mobile, i.e., if they can move in the soil profile in dissolved form, they can eventually reach a surface body of water or underlying ground water, increasing the likelihood of human and animal exposure to metals. Solubility of metal-containing phases is considered to be the main factor affecting metal mobility in contaminated soils (McGowen and Basta, 2001; Carrillo-González et al., 2006).

Soil solution composition is subject to changes during transport from the field to laboratory, due to aeration, loss of CO₂ and temperature variations, that all influence precipitation and sorption processes (McBride, 1994). Saturated paste extracts have been widely used as proxies of soil solutions (Sparks et al., 1996; Sparks, 2003), since it is easier and less time consuming to collect soil samples and to proceed to extractions in the laboratory than to monitor soil solutions and measure non conservative parameters directly in the field.

The aim of this study was to evaluate the effectiveness of saturated paste extracts for the assessment of Cu mobility in soils contaminated by atmospheric fallout. Soils at the study site are acid, coarse textured

and poor in organic matter. Under such conditions, adsorptive processes are expected to be relatively low while movement of dissolved copper in the soil profile is expected to be high. Copper mobility was evaluated in soil solutions collected by means of perforated plastic bottles installed in situ.

Lime and other alkaline materials are known to reduce Cu dissolution in contaminated soils if pH did not exceed 8.5 (Oste et al., 2001; Lombi et al., 2003; Ruttens et al., 2006). The effect of liming is based on the formation of new particles, i.e. precipitation or coprecipitation of metals, or on the binding to the surface of existing soil particles, i.e., metal sorption (McBride, 1994; Ma et al., 2006). Soil organic matter is known to adsorb Cu strongly (McBride, 1994; Baker and Senft, 1995). However, soluble organic ligands can increase Cu mobility in soils (Martínez and McBride, 1999; Ruttens et al., 2006). Therefore, this study will also discuss the effect of liming and organic matter addition on Cu mobility in the contaminated soils.

2. Materials and methods

2.1. Study area

Soils of the Puchuncaví valley in the coastal area of central Chile have been exposed to emissions of sulfur dioxide and metal-rich

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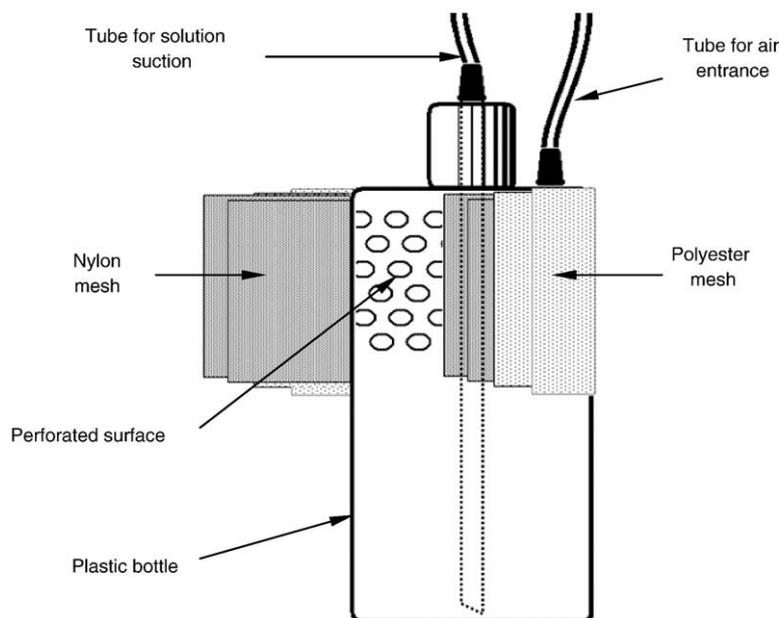


Fig. 1. Scheme of the soil solution sampler used in the study.

particles from the Ventanas Cu smelter since 1964. Environmental regulations that limit gaseous and particulate matter emissions were lacking until 1991; however, the emissions were only reduced significantly starting in 1999, i.e., after 35 years of production (Folchi, 2006).

Nowadays, the soils in the areas near the smelter are acidic (pH in water = 4.7) and metal-contaminated (up to 680 mg Cu/kg soil) (Ginocchio, 2000; Ginocchio et al., 2004). In smelter dust, Cu is present as chalcocyanite (CuSO_4), a highly soluble compound. Addition of smelter dust to soils results in their acidification because it exhibits extremely acid pH (around 2–3) in solution (Ginocchio et al., 2006), due to sulphuric acid. Soil acidification, in turn, may considerably increase Cu dissolution in contaminated soils (Sauvé et al., 2000).

The Los Maitenes study site is approximately 2 km east of the Ventanas smelter and was chosen because metal concentrations in this locality were reported to be the greatest in the Puchuncaví valley (González and Bergqvist, 1986). Smelting activities have been shown to increase soil concentrations of Cu, Zn, Pb, and Cd (González and Bergqvist, 1986; González and Ite, 1992; Ginocchio, 2000; Ginocchio et al., 2004). However, this study focused on the Cu mobility.

Based on the preliminary analyses of several soils at Los Maitenes, total Cu concentrations in this locality varied in the 92–872 mg/kg range (median of 550 mg/kg) (González et al., 2008). Two plots were selected for the study. The first plot was non-agricultural and sparsely-vegetated. It was considered to be representative of the non-agricultural area based on the preliminary survey. Another plot was a land used for crop production for several decades. This plot will be referred to as “farm” in the further discussion. These two plots were less than 10 m apart.

In April 2006, the non-agricultural plot was horse-plowed and divided into 4 sub-plots of about 25 m² each. Three sub-plots were used without any treatment (will be referred to as “control 1, control 2, and control 3”), while calcium hydroxide was mixed into the soil on the fourth sub-plot at 600 g/m² (will be referred to as “liming” or “lime treatment”). To avoid cross contamination, plastic separators were introduced to a depth of 30 cm between the sub-plots.

Based on personal communication with the farmer, cow and horse manure were annually applied during several decades on the

cultivated plot while inorganic fertilizers have never been used. The farm was horse-plowed annually and irrigated with well water. To avoid cross contamination, plastic separators were introduced to a depth of 30 cm between the studied farm plot (about 25 m²) and the rest of the farm.

2.2. Determination of Cu mobility in soils

To determine Cu mobility in the soils, one soil solution sampler per plot was installed in the soil at 30 cm depth, corresponding to the plow depth. Each soil solution sampler consisted of a plastic bottle that was perforated at its upper part to allow soil solution collection (Fig. 1). The perforations were covered by two layers of nylon and polyester mesh to prevent coarse particle entrance into the bottle. The

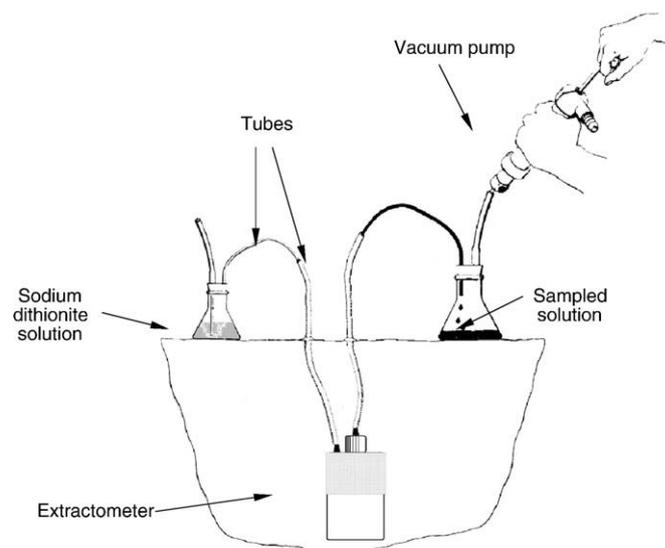


Fig. 2. Scheme of solution suction procedure.

Table 1
Selected properties of the studied soils.

Soil	Depth, cm	OM, %	pH	Total Cu, mg/kg	Sand, %	Silt, %	Clay, %	Textural class
Control 1	0–30	1.4	4.6	596	74	13	13	Sandy loam
	30–45	1.2	6.4	45	42	18	40	Sandy clay
	45–60	0.6	7.2	31	58	15	27	Sandy loam
Control 2	0–30	1.8	5.5	578	nd	nd	nd	–
Control 3	0–30	1.0	5.3	307	65	17	18	Sandy loam
Ca(OH) ₂ Farm	0–30	2.3	8.1	636	74	17	9	Sandy loam
	0–30	3.9	7.9	356	67	18	16	Sandy loam
	30–45	0.9	7.4	56	44	16	40	Sandy clay
	45–60	0.3	7.7	36	69	20	12	Sandy loam

OM = organic matter, nd = not determined. Values of pH were determined in the saturated paste extracts. Textural class is given according to Soil Survey Staff (2003).

soil solution sampler had two tubes. One was reaching the bottom of the bottle and was used for solution suction. Another was serving for air entrance to the bottle during solution suction. The solution obtained from the soil solution sampler will be referred to as “soil solution” in the further discussion.

To prevent solution reaction with oxygen, the air entering to the soil solution sampler during the sampling was bubbled through a solution composed of 25 ml of sodium dithionite (200 g/L) and 4 ml of sodium hydroxide (750 g/L) (Fig. 2) as proposed by Maître (1991) and Bourrié et al. (1999). The method is based on the following reaction (Charlot, 1966): $\text{Na}_2\text{S}_2\text{O}_4 + \text{O}_2 + \text{H}_2\text{O} = \text{NaHSO}_4 + \text{NaHSO}_3$. Based on the reaction stoichiometry, it was calculated that 25 ml of sodium dithionite react with 300 ml of oxygen that is equivalent to about 1.5 L of air. At the end of each sampling, both tubes of the soil solution sampler were sealed by adhesive tape to prevent oxygen entrance to the soil solution sampler.

Considering that rainfall occurs only in winter in central Chile (IGM, 2003), determination of Cu mobility in the soil was carried out from April 2006 until November 2006. It was based on the rain periodicity and was thus irregular. There were 5 days of precipitation during the study period: July 7 (5 mm), July 14 (73 mm), July 27 (82 mm), August 11 (28 mm), and October 14 (31 mm). Sampling was carried out the day following the rain event.

Immediately after the solution was collected from the soil solution sampler, pH, redox potential (Eh), and pCu^{2+} ($\text{pCu}^{2+} = -\log [\text{Cu}^{2+}]$, where $[\text{Cu}^{2+}]$ is the activity of free Cu^{2+}) were determined in the field using a portable instrument and glass, platinum, and copper ion-selective electrodes, respectively. The pH electrode was calibrated using reference pH solutions. Platinum combined electrode was verified by a reference solution of Eh = 470 mV. Readings of the platinum electrode were corrected to the standard hydrogen electrode

by adding 208 mV (Bates and Macaskill, 1978). The Cu ion-selective electrode was calibrated using Cu-iminodiacetic acid buffer solutions (Rachou et al., 2007).

Soil solutions were then transported to the laboratory and filtered through 0.2 μm filters. Concentration of dissolved organic carbon (DOC) was estimated according to Moore (1985) by visible spectrophotometer: $\text{DOC (mg/L)} = 45.05x + 1.803$, where x = absorbance at 330 nm. The solutions were then acidified (100 μL of concentrated HNO_3 per 10 mL of the solution) prior to analysis using atomic absorption spectrophotometry (AAS) on a GBC model 902 instrument.

The solution volume extracted by the soil solution samplers was insufficient for analysis in the case of all plots on July 7, the control 2 on July 14, and the control 3 on July 27 and August 11. Likewise, there was no sufficient sample volume for analysis of DOC and Cu in the case of controls 1 and 2 on October 14. The Cu concentrations were below the detection limit (50 $\mu\text{g/L}$) on July 14, July 27, and August 11 in the case of the control 1 and on July 14 in the case of the control 3.

2.3. Soil characterization

In August 2006, a sample of topsoil (0–30 cm) was taken from each of the 4 sub-plots and the farm. Subsoil samples (30–45 cm and 45–60 cm) were taken from the control 1 and the farm. The infiltration rate was determined in triplicate by the double-ring infiltrometer method (Brady and Weil, 2002).

The soil samples were processed by drying them at 60 °C, breaking aggregates in a granite mortar, and sieving them to obtain the fraction of <2 mm. Soils were characterized by routine methods. Organic matter was determined by oxidation with sodium dichromate and sulfuric acid (Sadzawka et al., 2006). Texture was determined by a simplified hydrometer method (Sheldrick and Wang, 1993).

Total Cu concentrations in the soils were determined by AAS following fine grinding of the samples in an agate mortar and their digestion with nitric–perchloric–hydrofluoric acid mixture (Maxwell, 1968; Jeffery, 1970).

The accuracy of the latter determination was assessed by analyzing reference materials of the International Atomic Energy Agency: river sediment GBW 07312 and lake sediment IAEA-SL-1. The reference values (in mg Cu/kg) were 1230 ± 12 and 30 ± 5.0 , respectively, while the determined values were 1250 ± 14 and 28.8 ± 0.7 , respectively. Thus, the deviations in the reference and determined values were less than 5%.

Saturated pastes were prepared and left to equilibrate overnight and were then extracted by vacuum filtration (Sadzawka et al., 2006). Values of pCu^{2+} and pH were determined as above. Concentrations of copper, potassium, sodium, calcium, magnesium, ammonium, sulphate, chloride, phosphate, and nitrate in the saturated paste extracts were determined by routine methods (Sadzawka et al., 2006) while the alkalinity was determined by the Gran method (Bourrié, 1976).

Table 2
Comparison of pH, pCu^{2+} , and Cu in saturated paste extracts and in the extractometers.

	pH		Cu, mg/L		pCu^{2+}		
	Extractometer	Saturated paste	Extractometer	Saturated paste	Extractometer	Saturated paste (determined)	Saturated paste (calculated)
Control 1	5.7–6.3	4.6	<0.05	13.4	8.1–8.7	4.2	3.9
Control 2	5.8–6.4	5.5	0.24	2.3	8.2–8.5	5.7	4.6
Control 3	5.8–6.4	5.3	<0.05–0.09	1.0	7.9–8.7	5.4	4.0
Ca(OH) ₂	5.6–6.2	8.1	0.05–0.21	4.3	7.6–8.4	9.2	6.2
Farm	6.3–7.1	7.9	0.26–0.34	1.7	9.2–10.0	10.2	6.5

Calculation of pCu^{2+} values in the saturated paste extracts was performed using the Visual MINTEQ program (Gustafsson, 2005) and considered composition of inorganic ions only (Appendix A).

The extracts were filtered through 0.2 µm cellulose acetate syringe filters and acidified as mentioned above prior to AAS analyses of cations. In addition, a sample of irrigation water was analyzed in the same way as the saturated paste extracts. Chemical speciation in the saturated paste extracts was calculated using the Visual MINTEQ program (Gustafsson, 2005).

All soil analyses were performed in duplicate and average values are shown in Tables 1 and 2. The deviations in the values obtained from the duplicate were less than 10%.

3. Results and discussion

3.1. Soil characterization

The soils corresponded to Entisols (Soil Survey Staff, 2003). The topsoils (0–30 cm) are sandy loam (Table 1). This coarse texture implies low nutrient availability (Ginocchio, 2000) and limited water holding capacity. However, the subsoils at 30–45 cm are sandy clays, while the subsoils at 45–60 cm are sandy loams. The initial infiltration rate (at 5 min) was 230 ± 37 mm/h; a stable infiltration rate of 50 ± 13 mm/h was reached at 40 min.

Total Cu concentrations in the topsoils were in the range of 310–640 mg/kg (Table 1). In comparison, total Cu concentrations in topsoils in Valle Alegre and Maitencillo, located about 15 km south-east and 12 km north from Los Maitenes, varied in the range of 50–85 mg/kg (Isabel González, personal communication). Thus, the relatively-large Cu concentrations determined in Los Maitenes suggest an anthropogenic input from the Ventanas smelter.

Total Cu concentrations decreased considerably with depth (at 30–60 cm) and were in the 30–60 mg/kg range. Similar total Cu distribution with depth was reported by Ginocchio et al. (2004) in a location approximately 2 km south-east of the smelter. Thus, the anthropogenic inputs of the Ventanas smelter is restricted to the topsoil (up to 30 cm) while the subsoil seems to remain unaffected.

It could be argued that the relatively-large topsoil Cu concentrations at Los Maitenes can be attributed to a geochemical Cu abundance in the area. However, Cu mines are absent in the Puchuncaví valley (Lara and Romo, 2002). The Ventanas smelter was owned by the ENAMI (Empresa Nacional de Minería) from the date of its construction in 1964 until 2005. Since 2005, the smelter is owned by the CODELCO (Corporación Nacional del Cobre de Chile) (Folchi, 2006). The ENAMI was purchasing Cu concentrates for smelting from small and medium mines located elsewhere in Chile (Valenzuela et al., 2003). The CODELCO processes their own copper concentrates, e.g., from the Andina mining complex located in the high Andes (Lara and Romo, 2002). Thus, the relatively-large topsoil copper concentrations in Los Maitenes are attributed to historic emissions of metal-rich particles from the Ventanas smelter.

Topsoil organic matter concentrations were in the range of 1.0–2.3% in the controls and lime treatment as compared to 3.9% in the farm (Table 1). Organic matter concentrations decreased with depth.

The control topsoils exhibited pH values in the 4.6–5.5 range (Table 1) while subsoil pH at the control 1 plot was near neutral. Similar pH distribution with depth was reported by Ginocchio et al. (2004) in a location approximately 2 km to the south-east of the smelter.

Liming increased topsoil pH to 8.1 (Table 1). The farm topsoil and subsoil exhibited similar pH values in the range of 7.4–7.9. Based on personal communication with the owner of the farm plot, this soil has never been limed during at least 4 decades. However, the well water used for irrigation exhibited a pH of 8.6 and an alkalinity of 2.54 mmol_c/L. Thus, most probably, irrigation water partly neutralizes the acid atmospheric depositions produced by the Ventanas smelter in the farm topsoil. As alkalinity of the water is positive, pH tends to increase when water is evaporated (Bourrié,

1976). Moreover, soil organic matter is known to act as a pH buffer (McBride, 1994). Cow and horse manure applied annually to the farm soil during at least 4 decades most likely were buffering the topsoil pH.

3.2. Dissolution and activity of copper as estimated by saturated paste extracts

Free Cu²⁺ activities in the saturated paste extracts decreased with soil organic matter concentrations (Fig. 3a). Concentrations of DOC are expected to increase with soil organic matter concentrations. The complex stability constants of Cu²⁺ with organic ligands are the

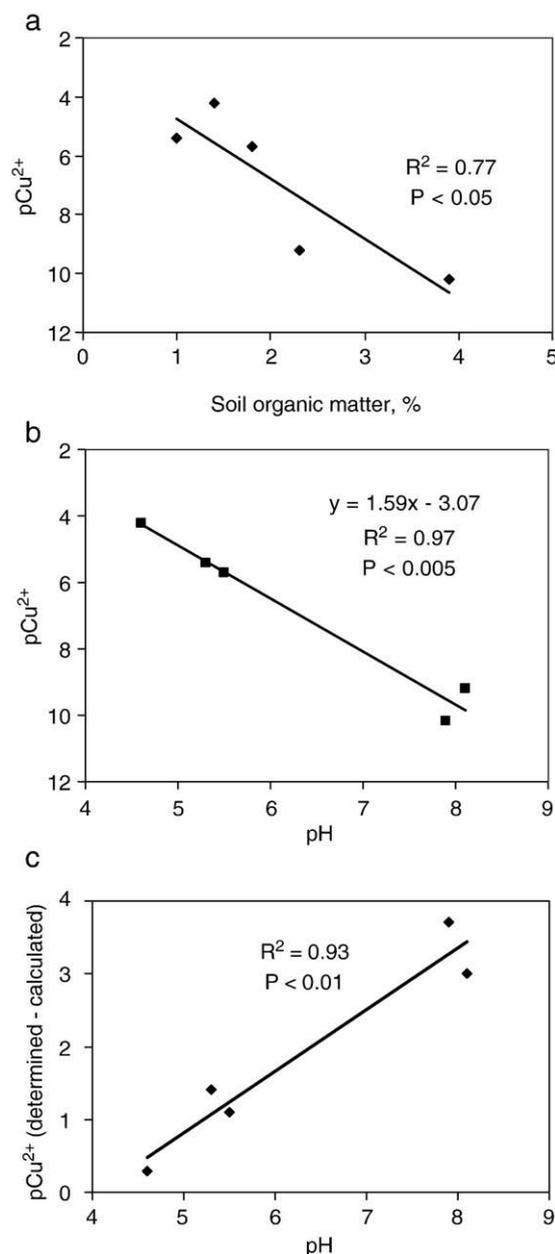


Fig. 3. Correlations between (a) pCu²⁺ and soil organic matter, (b) pCu²⁺ and pH, and (c) the difference between the determined and calculated pCu²⁺ values and pH. Values of pH and pCu²⁺ were determined in the saturated paste extracts. Calculation of pCu²⁺ values in the saturated paste extracts was performed using the Visual MINTEQ program (Gustafsson, 2005) and considered composition of inorganic ions only (Appendix A).

greatest among the divalent cations (NIST, 1998; IUPAC, 2000). Thus, Cu in the solution is expected to be almost entirely complexed by organic ligands, in agreement with previous reports (Sauvé et al., 1997; Sauvé, 2003).

Not surprisingly, free Cu^{2+} activities decreased in the saturated paste extracts following an increase in pH (Fig. 3b). This is probably due to the competition between protons and Cu^{2+} ions for ligands (L^{2-}) on soil solids, i.e., CuL partly dissociates when pH decreases. For the reaction $\text{CuL} + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{L}$, one would obtain: $\text{pCu}^{2+} - 2\text{pH} - \log [\text{H}_2\text{L}]/[\text{CuL}] = \text{p}K_2$, and for the reaction $\text{CuHL} + \text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{L}$, one would obtain: $\text{pCu}^{2+} - \text{pH} - \log [\text{H}_2\text{L}]/[\text{CuHL}] = \text{p}K_1$. If one considers as approximately constant the ratios of activities in brackets, one would expect a slope in between 1 and 2 in the correlation between pH and pCu^{2+} , as is obtained (Fig. 3b).

Values of pCu^{2+} determined in the saturated paste extracts were greater than the pCu^{2+} values calculated using the chemical speciation model (Table 2). Since only the complexation by the inorganic ions was considered for the calculation, the difference must be due to Cu complexation with organic ions. Calculations for complexation with organic ions were not carried out because DOC concentrations were not estimated in the saturated paste extracts.

The difference between the determined and calculated pCu^{2+} values increased with pH (Fig. 3c), suggesting that the proportion of organic complexes increases with pH. The solubility of soil organic matter is also known to increase with pH (McBride, 1994). Thus, increase in the difference between the determined and calculated pCu^{2+} values with pH is most probably due to the increase in DOC concentrations.

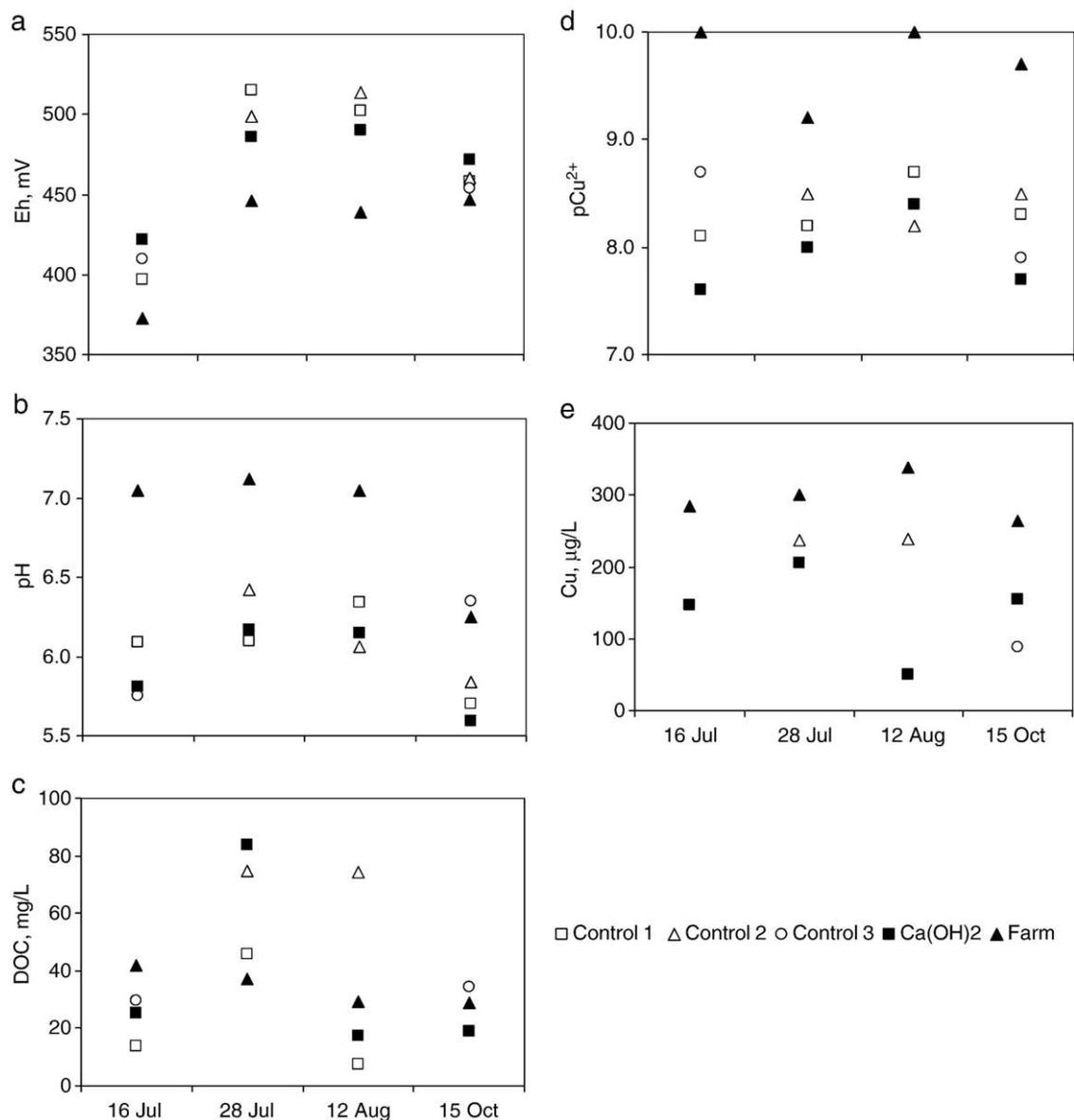


Fig. 4. Seasonal dynamics of (a) redox potential, Eh, (b) pH, (c) dissolved organic carbon, DOC, (d) pCu^{2+} , and (e) copper in the soil solution of the soils. The solution volumes extracted by soil solution samplers were insufficient for analysis in the case of the control 2 on July 14, and in the case of the control 3 on July 27 and August 11. Likewise, there was no sufficient sample volume for analysis of DOC and Cu in the case of controls 1 and 2 on October 14. The concentrations of Cu were below the detection limit ($50 \mu\text{g/L}$) in the case of the control 1 on July 14, July 27, and August 11, and in the case of the control 3 on July 14.

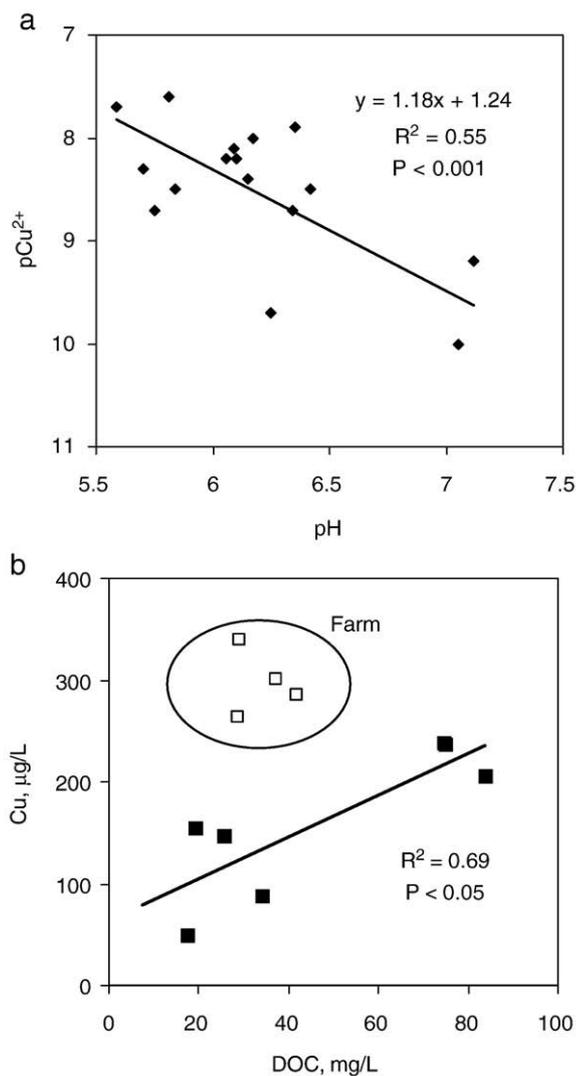


Fig. 5. Correlations between (a) pH and pCu²⁺, and (b) Cu in the solution and dissolved organic carbon (DOC). Data for the soil solutions obtained by mean of soil solution samplers (Figs. 1 and 2). The farm soil was not included in the regression in (b).

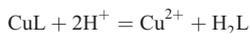
McBride et al. (1997) developed a semi-empirical equation from metal complexation theory which relates the metal activity of soil solutions to the soil's pH, organic matter concentration (OM) and total metal concentration (M_T). The equation has the following form: $pM = a + b \text{ pH} + c \log M_T + d \log \text{ OM}$, where pM is the negative logarithm (to base 10) of the metal activity, and a, b, c, and d are coefficients that can have positive or negative sign.

On metal-contaminated sites, concentrations of total soil metal and soil organic matter may be auto-correlated due to reduction of soil organic matter decomposition by metal contamination (Sauvé, 2006). In our experimental site, however, correlation between total soil copper and soil organic matter on non-agricultural sub-plots was not significant ($p > 0.05$). Thus, both of these variables were included when applying the approach of McBride et al. (1997) to our data. The following equation with all variables being significant ($p < 0.05$) was obtained ($R^2 = 0.999$, $n = 5$): $p\text{Cu}^{2+} = 4.74 - 2.45 \log \text{ Cu}_T + 2.78 \log \text{ OM} + 1.27 \text{ pH}$, where pCu²⁺ and pH were determined in saturated paste extracts.

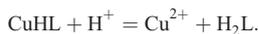
McBride et al. (1997) suggested that free Cu²⁺ activity in the soil solution is determined by the competition of Cu²⁺ ions and protons for ligands of soil organic matter by the following reaction: $\text{CuL} + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{L}$. This reaction implies the pH coefficient of 2 in the relationship between

pCu²⁺ and pH. Lindsay (1979) also set the pH coefficient of 2 in this relationship. Our data, however, suggest the pH coefficient of 1.27. Similarly, McBride et al. (1997) reported the pH coefficients of 1.37 and 1.6 for different data sets. Rachou et al. (under review) used a large database with more than 297 samples from 15 sites all over the world, with soil pH in the range of 3.5 to 7.5. The authors reported a similar pH coefficient of 1.36 in the relationship between pCu²⁺ and pH.

As discussed above, it is likely that two simultaneous reactions occur due to partial dissociation of CuL when pH decreases:



and



Thus, one would expect a slope in between 1 and 2 in the correlation between pH and pCu²⁺, as is obtained in the present study and in the above-mentioned studies.

Similarly to the equation for metal activity, the equation for soluble metal concentration (M_S) in water (or diluted salt) extracts has the following form (McBride et al., 1997): $M_S = a + b \text{ pH} + c \log M_T + d \log \text{ OM}$. However, in the present study, concentrations of Cu in the saturated paste extracts were not well predicted by this equation. This, most probably, is due to a relatively small number of samples ($n = 5$) used in the present study. In contrast, in the study of González et al. (2008), a larger number of samples was used ($n = 13$) and a statistically-significant relationship was found between Cu dissolution in salt extracts and total soil Cu and pH for non-agricultural soils at Los Maitenes.

3.3. Eh as directly measured in soil solutions

All measured Eh values were in the range of 350–550 mV (Fig. 4a) that is typical for aerobic soils (McBride, 1994). This suggests that the soils were not waterlogged even after the very strong rains of July 14 (73 mm) and July 27 (82 mm). This is most probably due to coarse texture of the soils that allow rapid water infiltration (50 ± 13 mm/h) without generation of reducing conditions. Thus, changes in redox conditions seem to be of minor importance in the soils.

3.4. Effect of liming and organic matter addition on copper mobility

Although only one soil solution sampler was installed per plot, the effect of liming and organic matter addition on copper mobility can be evaluated based on 4 samplings performed during the study period. In the case of control plots with Cu concentrations below the detection limit, these concentrations were assumed to be at the detection limit (50 μg/L) for the purpose of comparison to lime and farm plots. In some cases, however, it was not possible to apply statistical procedures due to insufficient sample volume extracted by the soil solution samplers.

Studies of Martínez and McBride (1999), Kiikkila (2003), and Ruttens et al. (2006) suggest that organic matter addition to the soil can increase the amount of soluble organic ligands and eventually mobilize Cu. Present findings also suggest that DOC is an important factor controlling Cu mobility in the non-agricultural soils. Although the differences between the plots were statistically non-significant (Tukey test, $p > 0.05$) in the case of DOC (Fig. 4c, Table 2), soil solution concentrations of Cu in the non-agricultural soils (controls and lime plots) increased with DOC concentrations (Fig. 5b). Concentrations of Cu in the soil solution significantly differed on the farm plot in comparison to other plots (Tukey test, $p < 0.001$). Specifically, Cu concentrations in the solution were in the range of 0.26–0.34 mg/L in the case of the farm plot and <0.05–0.24 mg/L in the case of all other plots (Fig. 4e, Table 2). This effect is attributed to complexation of Cu by organic ligands. However, the

farm soil did not exhibit the same trend in the relationship between the DOC and Cu in the soil solution (Fig. 5b), possibly due to a different composition and structure of the organic ligands in the farm soil versus the non-agricultural soils.

Values of free Cu^{2+} activities were significantly lower on the farm plot in comparison to all other plots (Tukey test, $p < 0.001$). Specifically, pCu^{2+} varied in the 9.2–10.0 range in the case of the farm plot in comparison to the range of 7.6–8.7 in the case of all other plots (Fig. 4d, Table 2). This effect is attributed to higher pH values in the soil solution on the farm plot in comparison to other plots (Fig. 4b) and, as discussed in earlier, through competition between protons and Cu^{2+} ions for ligands. Similar to saturated paste extracts, free Cu^{2+} activities in the soil solutions decreased with increasing pH (Fig. 5a) and could be explained by competition between protons and Cu^{2+} ions for ligands. The slope in between 1 and 2 in the correlation between pH and pCu^{2+} is consistent with this mechanism.

In summary, the largest concentrations of Cu in the soil solution while the smallest free Cu^{2+} activities were observed on the farm plot. The concentration of dissolved organic carbon was the major factor controlling the mobility of copper in the soils while soil pH was the major factor controlling the free Cu^{2+} activity in the soil solution.

3.5. Copper mobility: soil solutions versus saturated paste extracts

As mentioned above, metal concentration in saturated paste extracts (or water or salt extracts) is a measure of solubility of metal-containing phases in the soil (McBride et al., 1997) and thus is expected to be useful for assessment of metal mobility in the soil profile. However, Cu concentrations in the soil solutions were considerably smaller than those in the saturated paste extracts for all soils (Table 2). Likewise, values of pH and pCu^{2+} of the soil solutions were larger than in the saturated paste extracts for the control soils, while the reverse was observed in the case of the limed and farm plots.

The above observations are most probably due to coarse texture of the soils that allow rapid water infiltration at an initial rate of 230 ± 37 mm/h reaching a stable infiltration rate of 50 ± 13 mm/h at 40 min. This rapid water infiltration, in turn, does not allow the equilibrium between the rain water and the soil constituents to be reached. As a consequence, this limits the potential for Cu leaching to the subsoil and soil acidification is also limited during the sparse rain events.

This result is consistent with the data on total Cu and pH distribution with depth in the soils (Table 1) and the findings of Ginocchio et al. (2004). These data suggest that the anthropogenic inputs of the Ventanas smelter, with respect to increase in Cu concentrations and acidification, is restricted to the topsoil (up to 30 cm) while the subsoil remains unaffected.

The present results suggest that metal dissolution, measured by means of saturated paste extracts, is not representative of metal mobility as it occurs in situ for contaminated soils. The saturated paste extracts overestimate the metal mobility as it occurs in situ for contaminated soils.

3.6. Evaluation of environmental importance of copper mobility in the soils

In order to estimate the importance of the metal leaching on a contaminated site, Ruttens et al. (2006) used an option comparing the metal concentration in the soil solution percolating through contaminated soils versus the “Flemish intervention guideline for groundwater clean up”. In the case of Cu, this latter standard established the threshold concentration at 0.1 mg/L (citation in Ruttens et al., 2006).

Similarly, the Chilean guideline for irrigation water (Norma Chilena Oficial N° 1333, 1978) establishes a threshold concentration of 0.2 mg Cu/L. Concentrations of Cu in some of the soil solutions exceeded the Chilean guideline. Although these Cu concentrations will be diluted by the receiving groundwaters, acute toxicity of Cu to aquatic organisms is known to occur at much smaller Cu concentrations, in the range of 6.9–10.8 $\mu\text{g/L}$ for freshwater and 2.1–16.1 $\mu\text{g/L}$ for saltwater, depending on species (Adriano, 2001).

Free cupric ion (Cu^{2+}) is generally considered as the most bioavailable form of Cu, especially to aquatic organisms (Ma et al., 1999; Adriano, 2001). Studies indicated that this is also the case in soils. Use of free Cu^{2+} activity as an indicator of bioavailability is useful because Cu^{2+} integrates the influence of various soil chemical characteristics. For example, Sauv e et al. (1998) concluded that, in a majority of cases, free metal activity improves the prediction for toxic effects on crops, soil organisms, or soil microbial processes. In a meta-analysis, the authors reported a pCu^{2+} value of 7.2 ± 1.7 as a limit of risk for 50% inhibition of measured biological parameters.

By applying the latter pCu^{2+} value to our soils, the farm plot would be considered as the safest as it exhibited values of pCu^{2+} in the soil solution in the range of 9.2–10.0 while pCu^{2+} values on other plots were in the range of the range of 7.6–8.7. Thus, organic amendments are a mean of lowering Cu toxicity in the contaminated soils.

However, the present findings and reports of Mart nez and McBride (1999), Kiikkil a (2003), and Ruttens et al. (2006) suggest that organic amendments may increase Cu mobility and leaching in contaminated soils. Further studies are needed to develop methodologies on how to minimize Cu leaching from the contaminated soils when organic amendments are applied.

4. Conclusions

- 1) Copper concentrations in the soil solutions were considerably smaller than those in the saturated paste extracts for all soils. Thus, saturated paste extracts were not a good proxy of soil solutions for short duration and intense rain events and not a good mean of assessing copper mobility in contaminated soils for our experimental site. In situ soil solution sampling using simple and low-cost devices, such as those used in this study, is a better mean for assessment of metal mobility in contaminated soils in comparison to saturated paste extracts.
- 2) The coarse texture of the soils allows rapid water infiltration that does not allow the equilibrium between the rain water and the soil constituents to be reached. As a consequence, copper leaching to the subsoil and its acidification is limited during rain episodes. Thus, the anthropogenic inputs of the Ventanas smelter, with respect to increase in copper concentrations and acidification, is restricted to topsoil (up to 30 cm) while the subsoil appears to remain largely unaffected.
- 3) The concentration of dissolved organic carbon was the major factor controlling the mobility of copper in the soils while soil pH was the major factor controlling the free Cu^{2+} activity in the soil solution.

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Appendix A. Concentrations of cations and anions in the saturated paste extracts of the studied soils (mmol_c/L)

Sample	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Sum of cations	Alkalinity	SO ₄ ²⁻	Cl ⁻	H ₂ PO ₄ ⁻	NO ₃ ⁻	Sum of anions
Control 1	0.79	1.75	3.70	1.48	0.39	8.11	0.00	4.69	2.64	0.01	0.41	7.75
Control 2	0.36	0.57	2.72	0.67	0.29	4.60	0.31	1.18	0.31	0.08	0.07	1.95
Control 3	0.25	0.74	2.31	1.55	0.05	4.89	0.17	1.16	0.43	0.03	0.03	1.82
Ca(OH) ₂	0.53	0.46	11.44	0.93	0.00	13.36	6.26	5.15	0.05	0.04	0.01	11.51
Farm	9.06	5.02	16.43	6.58	0.23	37.32	9.38	8.02	4.99	0.71	12.01	35.11

References

- Adriano, D.C., 2001. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risk of Metals. Springer-Verlag, New York, NY, 867 pp.
- Baker, D.E., Senft, J.P., 1995. Copper. In: Alloway, B.J. (Ed.), Heavy Metals in Soils. Blackie Academic & Professional, London, UK, pp. 179–205.
- Bates, R.G., Macaskill, J.B., 1978. Standard potential of the silver–silver chloride electrode. *Pure and Applied Chemistry* 50, 1701–1706.
- Bourrié, G., 1976. Relations entre le pH, l'alcalinité, le pouvoir tampon et les équilibres de CO₂ dans les eaux naturelles. *Science du Sol* 3, 145–159.
- Bourrié, G., Trolard, F., Génin, J.-M.R., Jaffrezic, A., Maître, V., Abdelmoula, M., 1999. Iron control by equilibria between hydroxy-green rusts and solutions in hydromorphic soils. *Geochimica et Cosmochimica Acta* 63, 3417–3427.
- Brady, N.C., Weil, R.R., 2002. The Nature and Properties of Soils. Pearson Education, Upper Saddle River, NJ, USA.
- Carrillo-González, R., Šimunek, J., Sauvé, S., Adriano, D., 2006. Mechanisms and pathways of trace element mobility in soils. *Advances in Agronomy* 91, 111–178.
- Charlot, G., 1966. Les méthodes de la chimie analytique: Analyse quantitative minérale. Masson et Cie Editeurs, Paris, France, 1023 pp.
- Folchi, M., 2006. Historia ambiental de las labores de beneficio en la minería de cobre en Chile, siglos XIX y XX. Tesis de doctorado, Departamento de Economía y de Historia Económica, Universidad Autónoma de Barcelona.
- GINOCCHIO, R., 2000. Effects of a copper smelter on a grassland community in the Puchuncavi valley, Chile. *Chemosphere* 41 (1–2), 15–23.
- GINOCCHIO, R., CARVALLO, G., TORO, I., BUSTAMANTE, E., SILVA, Y., SEPULVEDA, N., 2004. Micro-spatial variation of soil metal pollution and plant recruitment near a copper smelter in central Chile. *Environmental Pollution* 127 (3), 343–352.
- GINOCCHIO, R., et al., 2006. Agricultural soils spiked with copper mine wastes and copper concentrate: implications for copper bioavailability and bioaccumulation. *Environmental Toxicology and Chemistry* 25 (3), 712–718.
- González, S., Bergqvist, E., 1986. Evidencias de contaminación con metales pesados en un sector del secano costero de la V Región. *Agricultura Técnica (Chile)* 46, 299–306.
- González, S., Ite, R., 1992. Acumulación metálica en suelos del área bajo influencia de las chimeneas industriales de Ventanas (provincia de Valparaíso, V Región). *Agricultura Técnica (Chile)* 50, 214–219.
- González, I., Muena, V., Cisternas, M., Neaman, A., 2008. Acumulación de cobre en una comunidad vegetal afectada por contaminación minera en el valle de Puchuncavi, Chile central. *Revista Chilena de Historia Natural* 81, 279–291.
- Gustafsson, J.P., 2005. Visual MINTEQ, version 2.31. <http://www.lwr.kth.se/english/OurSoftware/Vminteq/>.
- IGM, 2003. Atlas Geográfico para la Educación. Instituto Geográfico Militar de Chile, Santiago, Chile.
- IUPAC, 2000. IUPAC stability constants database. Release 5. International Union of Pure and Applied Chemistry and Academic Software. <http://www.acadsoft.co.uk>.
- Jeffery, P.G., 1970. Chemical Methods of Rock Analysis. Pergamon Press, Oxford.
- Kiikkilä, O., 2003. Heavy-metal pollution and remediation of forest soil around the Harjavalta Cu–Ni smelter, in SW Finland. *Silva Fennica* 37 (3), 399–415.
- Lara, L., Romo, L., 2002. Atlas de Faenas Mineras: Minas y Plantas de las Regiones V, VI y XIII. Mapas y Estadísticas de Faenas Mineras de Chile. Servicio Nacional de Geología y Minería, Santiago, Chile.
- Lindsay, W.L., 1979. Chemical Equilibria in Soils. John Wiley & Sons, New York, NY, 412 pp.
- Lombi, E., Hamon, R.E., McGrath, S.P., McLaughlin, M.J., 2003. Lability of Cd, Cu, and Zn in polluted soils treated with lime, beringite, and red mud and identification of a non-labile colloidal fraction of metals using isotopic techniques. *Environmental Science & Technology* 37 (5), 979–984.
- Ma, H., Kim, S., Cha, D., Allen, H., 1999. Effect of kinetics of complexation by humic acid on toxicity of copper to *Ceriodaphnia dubia*. *Environmental Toxicology & Chemistry* 18, 828–837.
- Ma, Y., Lombi, E., Oliver, I., Nolan, A., McLaughlin, M., 2006. Long-term aging of copper added to soils. *Environmental Science & Technology* 40, 6310–6317.
- Maître, V., 1991. Géochimie des eaux libres extraites de sols hydromorphes sur granite dans le Massif Armoricaïn: Mobilité du fer et dynamique saisonnière. Université Paris VI, Paris, France, 203 pp.
- Martínez, C.E., McBride, M.B., 1999. Dissolved and labile concentrations of Cd, Cu, Pb, and Zn in aged ferrihydrite-organic matter systems. *Environmental Science & Technology* 33 (5), 745–750.
- Maxwell, J.A., 1968. Rock and Mineral Analysis. Interscience Publishers, New York.
- McBride, M.B., 1994. Environmental Chemistry of Soils. Oxford University Press, New York, NY.
- McBride, M., Sauvé, S., Hendershot, W., 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science* 48 (2), 337–346.
- McGowen, S.L., Basta, N.T., 2001. Heavy metal solubility and transport in soil contaminated by mining activities. In: Selim, H.M., Sparks, D.L. (Eds.), Heavy Metals Release in Soils. Lewis Publishers, Boca Raton, FL, USA, pp. 89–107.
- Moore, T.R., 1985. The spectrophotometric determination of dissolved organic carbon in peat waters. *Soil Science Society of America Journal* 49, 1590–1592.
- NIST, 1998. NIST critically selected stability constants of metal complexes database, Version 6. U.S. Department of Commerce, Gaithersburg, MD.
- Norma Chilena Oficial N° 1333, 1978. Requisitos de calidad del agua para diferentes usos. Diario Oficial de la República de Chile, Santiago, Chile, 22 de mayo de 1978.
- Oste, L.A., Dolfing, J., Ma, W.C., Lexmond, T.M., 2001. Effect of beringite on cadmium and zinc uptake by plants and earthworms: more than a liming effect? *Environmental Toxicology and Chemistry* 20 (6), 1339–1345.
- Rachou, J., Gagnon, C., Sauvé, S., 2007. Use of an ion-selective electrode for free copper measurements in low salinity and low ionic strength matrices. *Environmental Chemistry* 4, 90–97.
- Rachou, J., Neaman, A., and Sauvé, S., under review. Modelling soil solution free Cu²⁺ using a solid phase-controlled soil ligand model and simple semi-empirical regressions. *Environmental Science & Technology*.
- Ruttens, A., Colpaert, J.V., Mench, M., Boisson, J., Carleer, R., Vangronsveld, J., 2006. Phytostabilization of a metal contaminated sandy soil. II: Influence of compost and/or inorganic metal immobilizing soil amendments on metal leaching. *Environmental Pollution* 144 (2), 533–539.
- Sadzawka, A., Carrasco, M.A., Grez, R., Mora, G., Flores, H., Neaman, A., 2006. Métodos de análisis recomendados para los suelos de Chile. Revisión 2006. Serie actas INIA N° 34. Instituto de Investigaciones Agropecuarias, Santiago, Chile, 164 pp.
- Sauvé, S., 2003. The role of chemical speciation in bioavailability. In: Naidu, R., Gupta, V., V.S.R., Kookana, R.S., Rogers, S., Adriano, D. (Eds.), Bioavailability, Toxicity and Risk Relationships in Ecosystems. Science Publishers Inc., Enfield, NH, USA, pp. 49–82.
- Sauvé, S., 2006. Copper inhibition of soil organic matter decomposition in a seventy-year field exposure. *Environmental Toxicology & Chemistry* 25, 854–857.
- Sauvé, S., McBride, M.B., Norvell, W.A., Hendershot, W.H., 1997. Copper solubility and speciation of *in situ* contaminated soils: effects of copper level, pH and organic matter. *Water, Air, and Soil Pollution* 100 (1–2), 133–149.
- Sauvé, S., Dumestre, A., McBride, M., Hendershot, W., 1998. Derivation of soil quality criteria using predicted chemical speciation of Pb²⁺ and Cu²⁺. *Environmental Toxicology and Chemistry* 17 (8), 1481–1489.
- Sauvé, S., Hendershot, W., Allen, H., 2000. Solid-solution partitioning of metals in contaminated soils: dependence on pH and total metal burden. *Environmental Science & Technology* 34, 1125–1131.
- Sheldrick, B.H. and Wang, C., 1993. Particle size distribution. In: Carter, M. (Editor), Soil Sampling and Methods of Analysis. Canadian Society of Soil Science, Lewis Publishers, Boca Raton, FL, USA, pp. 499–511.
- Soil Survey Staff, 2003. Keys to soil taxonomy. United States Department of Agriculture, National Resources Conservation Service, Washington, DC, USA.
- Sparks, D.L., 2003. Environmental Soil Chemistry. Academic Press, Amsterdam.
- Sparks, D.L. et al., 1996. Methods of Soil Analysis. Part III: Chemical Methods. Soil Science Society of America Book Series No. 5. Soil Science Society of America, American Society of Agronomy, Madison, WI.
- Valenzuela, A., Palacios, J., Cordero, D., Sánchez, M., 2003. The Chilean copper metallurgical industry: an update. The Minerals, Metals & Materials Society Annual Meeting, March 3–6, 2003, San Diego, CA, USA.
- Vangronsveld, J., Sterckx, J., Vanassche, F., Clijsters, H., 1995. Rehabilitation studies on an old nonferrous waste dumping ground: effects of revegetation and metal immobilization by beringite. *Journal of Geochemical Exploration* 52 (1–2), 221–229.