

Distribution of trace elements in soils surrounding the El Teniente porphyry copper deposit, Chile: the influence of smelter emissions and a tailings deposit

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Abstract In the area surrounding the El Teniente giant porphyry copper deposit, eight soil sites were sampled at three depth levels in the summer 2004. The sites were selected for their theoretical potential of being influenced by past SO₂ emissions from the smelter and/or seepage from a now idle tailings impoundment. The soil mineralogy, grain size distribution, total organic matter contents, major element composition, cation exchange capacity, and Cu, Mo, Pb, Zn, As and SO₄²⁻ concentrations were determined for all samples after nitric acid extraction and separate leaches by ammonium acetate (pH 7) and sodium acetate (pH 5). For water rinses, only Cu could be determined with the analytical set-up used. Cu and SO₄²⁻ enrichment in topsoils was found at six sites either downwind from the smelter or within the combined influence of the smelter and the tailings impoundment. Both elements were released partially by ammonium and sodium acetate extractions. Due to the scarce background trace element concentrations of soil and rock outside the immediate mine area, assessment of trace element mobility

for Mo, Zn, Pb and As was difficult. Arsenic was found to be concentrated in soil horizons with high smectite and/or organic matter contents. Mo appears to be linked to the presence of windblown tailings sediment in the soils. Mobilization of Mo, Zn, and As for the acetate extractions was minimal or below the detection limits for the AAS technique used. The presence of windblown tailings is considered to be an additional impact on the soils in the foothills of the El Teniente compound, together with the potential of acidity surges and Cu mobilization in topsoils after rainfalls. Two sites located at the western limit of the former SO₂ saturated zone with strongly zeolitized soils and underlying rock did not show any Cu or SO₄²⁻ enrichment in the topsoils, and remaining total trace element concentrations were below the known regional background levels.

Keywords Soil · Porphyry copper deposit · Tailings · Smelter · Chile

Introduction

The El Teniente (ET) giant porphyry copper deposit, owned and operated by the Chilean state-owned copper company CODELCO, is located 80 km south of Santiago de Chile, in a region where the key sources of employment and income are large as well as small-scale mining and agriculture. In mining, porphyry copper mining generates the most intensive land use due to large tailings production as well as SO₂ emissions during smelting (Dudka and Adriano 1997), and ET copper deposit is no exception. One hundred years of uninterrupted copper and molybdenum production (Boletín Minero 2004) by

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flotation and smelting has filled until 1986 the Barahona 1, Barahona 2 and Cauquenes tailings impoundments (CICA 1998, Dold and Fontboté 2001), located at a short distance from the processing facilities in the Andean foothills (Fig. 1). At present, tailings are being sent 86 km across the Central Valley to the Carén impoundment, which received an average input of 119,000 ton of sludge/day in 2004. The Caletones smelting facility is also located on the foothills close to the mine and has been in operation since 1922. During the last decade, the installation of electrostatic precipitators and two sulfuric acid plants have reduced the SO₂, As and particulate matter (PM 10) emissions by up to 90% (<http://www.sustentable.cl>) in response to decontamination plans developed in the early 1990s (DFL 185, 1995). Between 1992 and 1994, emissions reached up to 800,000 ton/year of SO₂ and 900 ton/year of As (SMHL 2000; Ecclestone 1996). Since 1997, due to an environmental law passed in Chile, compliance with Chilean air- and water-bound emission standards is now systematically monitored. However, there is no systematic monitoring of soil quality because legislative discussion is in progress, and thus most environmentally oriented soil studies contribute to the establishment of baseline values and contamination source diagnosis (e.g., Ahumada et al. 2004; De Gregori et al. 2003) and are usually performed on a reduced number of samples.

The present study evaluates the influence of eight decades of SO₂, As and metal emissions from the Caletones smelter as well as the local seepage from the now unused Barahona 1 tailings impoundment in eight soil sites within the ET mine compound. The SO₄²⁻, Cu, Zn, Mo, Pb and As levels are discussed with respect to soil mineralogy, underlying lithology and climatic–geographic conditions.

Background information

Geographical and climatic framework

The ET compound (Fig. 1) is located in the Andean foothills and is part of the main Andean chain morphological units. Processing plants, offices at Colón and the now idle tailing dams Barahona 1 and Barahona 2 are all located in the foothills formed by laharcic deposits of Pliocene–Quaternary age and the Cauquenes impoundment inserted in Early Miocene volcanic rocks. The mine adits and the old mining town Sewell (presently being refurbished as a museum and declared as a UNESCO heritage site) are located along the V-shaped valley of the Coya river, which cuts into the Andean main chain. The Caletones smelter is situated at the border between the two morphological units. The Coya River is a major tributary of the Cachapoal River, which provides much of the irrigation water for the Central Valley. Drainage of the Barahona twin impoundments and circumferentially captured seasonal water influx arrive at the Coya River through the deep-cut Barahona valley.

The aforementioned morphological units are also reflected in two climatic zones. For the Barahona and Colón sector (Fig. 1), average monthly temperatures fluctuate between 4.1°C in June and 15.5°C in January (CICA 1998) with an average annual rainfall of 675 mm. Evaporation during summer may exceed 200 mm/month. In an Andean setting, the upper Coya valley at the Sewell monitoring station receives an average annual rainfall of 858 mm, with intense snowfall during winter. Temperatures fluctuate between an average annual minimum of −5.8°C and an annual average maximum of 25.4°C (Codelco 2005a). Dominant wind directions are from the SW and NE, with local morphology strongly influencing

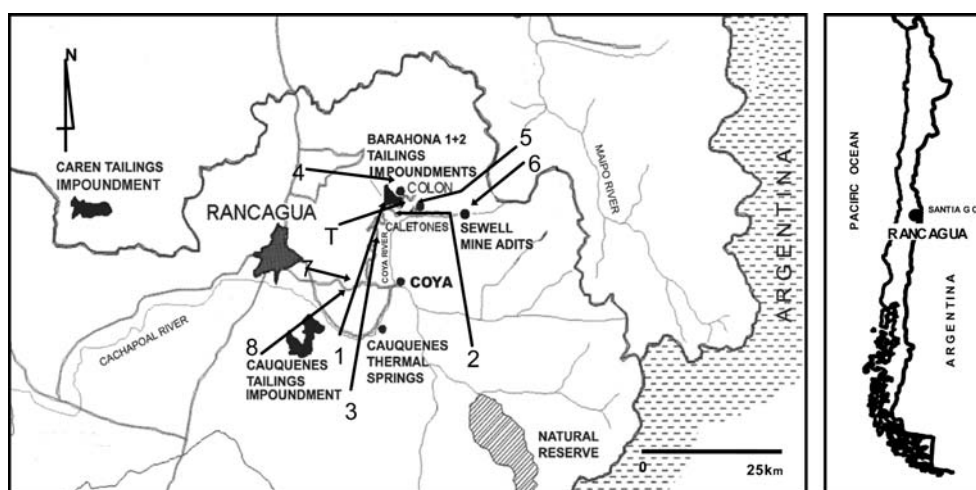


Fig. 1 Location of the study area and sampling sites

wind speeds (Codelco 2001). The soils surrounding the Barahona tailings impoundments are lithosols and fluvisols with little or no cover of vegetation, thus organic matter consists mainly of dead roots. Rock content can exceed 50% with slopes steeper than 27° (CICA 1998). Similar to most of the foothills located south of Santiago, this area is only used for seasonal extensive pasturing. Consequently, no systematic description and classification of soils is available, contrasting with the data available for the arable Central Valley (e.g. INIA 1985).

Geology, mining activity and the Barahona tailings impoundments

The ET porphyry copper deposit, with an annual production of 498.5×10^4 ton Cu and 3919 ton Mo in 2004 (Codelco 2005b), is the world's largest underground mine extracting ore from the Upper Tertiary Farellones Formation also described locally as the Teniente Volcanic Complex. The lithology comprises andesitic, rhyolitic and basaltic lava flows and continental sediments (Cares 2004). The principal ore minerals are chalcopryrite, bornite, molydenite, galena, tennantite/tetrahedrite, chalcocite and covellite (Camus 1975). More than 98% of the extracted gangue ending up in the tailings impoundments are: quartz, pyrite, hematite, K-feldspar, plagioclase, biotite, calcite, anhydrite, tourmaline, rutile, apatite, white mica, chlorite, epidote, kaolinite and montmorillonite (Dold and Fontboté 2001; INTEC 1985). The folded Coya Machalí Formation (Mid Tertiary), which underlies the Farellones Formation and forms the base rock of the Barahona tailings impoundments, is a sequence of fine-grained continental sediments with inter-bedded andesitic flows and pyroclastic deposits. In the main Andean chain, the valley bottoms and

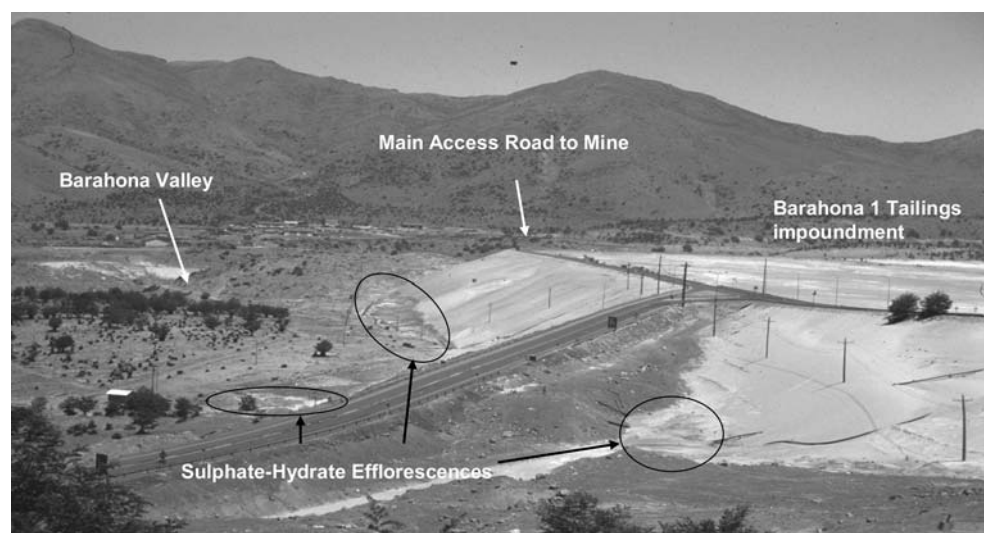
slopes are covered with Quaternary fluvio-glacial materials, whereas laharic and eolic sediments influence the valleys of the foothills.

The first report of mining at ET dates from the sixteenth century, but it was the Braden Copper Company that began continuous exploitation in 1905, first extracting exotic copper ore by heap leaching. Tailings deposited in the Barahona twin tailings impoundments comprise the gangue from 1917 to 1936, when an acid flotation circuit was used. The older Barahona 1 impoundment has received 15×10^6 m³ of material and the newer Barahona 2 deposit received 44×10^6 m³, covering a total surface of approximately 8.4 km². Feasibility studies on recovering part of the remaining 0.3% copper grade either by flotation or sulfuric acid leaching reported a pH of 4.1 and a <200 Tyler mesh fraction of above 59% for the tailings (INTEC 1985). The main supply road to the mine runs along the crown of the Barahona 1 dam (Fig. 2). For the Barahona dams, seepage at the bottom is estimated at 21 L/s with a pH of 2.85–3.10, copper levels of 245–1145 mg/L, and sulfate levels of 780–1528 mg/L (CICA 1998). Seepage drained in the past, with changing flow beds into the Barahona River; nowadays, this visible seepage is intercepted and recirculated to the tailings channel.

Sampling site selection

The present study is a pilot initiative, and sampling sites were selected according to their potential exposure to contamination sources in the past, the former SO₂ emissions of the Caletones smelter, and/or the seepage from the Barahona tailings deposit. Dust propagation from ore comminution is negligible since this process is largely performed underground and far away from the sampling

Fig. 2 View looking northeast of a part of the Barahona tailings impoundment with the main access road to the ET mine running along the crest of the dam



sites, except site 6, and consequently was not considered as a potential focus of contamination.

Except for the westernmost location (8), all sites (Fig. 1, Table 2) formed part at one stage of a SO₂ saturated area (CIMM 1995; Ministerio de Minería 1994) prior to installation of electrostatic precipitators in the Caletones smelter in the late 1990s. Table 1 summarizes the locations and their corresponding reference numbers in the text and Fig. 1.

Sites located at the base of the Barahona dam and within the Barahona valley potentially receive seeped fluids from the tailings impoundments. To avoid site contamination by materials or reagents related to ore processing, all the selected sites were located outside the direct influence of the processing plants or the smelter. The upper Coya Valley site (6) was chosen for its vicinity to the Sewell historic site and mine itself and also for its position in the “dead end” of a steep Andean valley.

Table 1 Details and sampling sites (sampling depths, organic matter content, weight percent of the <2 µm fraction, general whole soil and clay size fraction mineralogy)

Site number	Site name	Sample depth below the surface (cm)	Weight % of organic matter	Weight % of <2 µm size fraction	pH	Whole soil/rock mineralogy (XRD)				Clay mineralogy of <2 µm fraction			
						Q	fsp	mica	others	sm	chl	mica	ka
1a	Barahona, base of dam	0–20	4.56	3.8	4.23	xxx	x	x	hmt/goeth (x)		xx	xxx	
1b		20–30	4.51	2.5	3.95	xxx	x	x	hmt/goeth (x), chl (x)		xx	xxx	tr
1c		30–40	6.42	13.4	4.68	xxx	xx	x	ka (x), am	x		x	xx
1d		40–100	2.80	13.3	5.13	xxx	xxx	xxx	am (x), sm (x), ka (x)	tr		x	xx
2a	Barahona, seepage area	0–10	4.72	5.7	5.55	xxx	xx	xx	chl (x), am (x)	x	x	x	x
2b		10–50	3.85	2.8	4.30	xxx	xx	xx	chl (x), am (x)	x	tr	x	x
2c		50–100	5.20	16.3	6.01	xx	xxx	x	sm (xx), kao (x), am (x)	x		tr	xx
2d		100–150	12.19	9.2	5.83	xx	x	tr	ka (x), hmt/goeth, am (tr)	xxx		tr	x
3a	Barahona Valley	0–10	9.66	7.6	3.87	xxx	xx	tr	chl (tr), ka (tr), sm, am?	tr	x	tr	tr
3b		10–50	4.69	16.2	6.31	xx	xx	tr	sm (tr), ka (x), sul (tr), am?	x	tr	tr	tr
3c		50–130	3.66	4.3	6.32	x	xxx	tr	ka (x), hmt/goeth, sm (tr)	xx	tr	tr	tr
4a	Barahona East	0–12	10.16	6.6	3.62	xxx	xx	tr	hmt/goeth (x), ka (tr)	tr		tr	x
4b		12–47	3.39	11.6	6.14	xx	xx	tr	hmt/goeth (x), ka (tr)	tr		tr	x
4c		47–140	3.96	7.0	5.21	xx	xxx		hmt/goeth (x), sm (xxx)	tr		tr	x
5a	Quebrada La Frena	0–10	6.32	7.5	5.52		xx		hmt/goeth (x), zeo (x), sm (xxx)	xx			
5b		10–40	4.11	6.4	4.37	x	xx		sm (xxx), hmt/goeth?	xxx			
5c		40–110	6.49	11.3	5.23	x	x	tr	hmt/goeth (x), sm (xxx)	xxx			
6a	Adit mine 42	0–10	6.04	3.1	3.45	xxx	xx	x	chl (x)		xx	xx	
6b		10–70	3.11	5.0	4.62	xxx	xx	x	chl (xx), am (tr), hmt/goeth		xx	xxx	
7a	Maitenes	0–10	3.28	2.8	6.81	xxx	x	tr	sm (xx), ka (x), am (tr), hmt/goeth, zeo (tr), px (tr)	x		tr	xx
7b		10–70	2.65	11.7	6.42	xx	xx		sm (xx), ka (x), zeo (x), hmt/goeth (x)	xx			xxx
7c		70–120	3.57	16.2	6.59	x	x		zeo (xxx), sm (x), ka (x), hmt/goeth (x)	xxx			xxx
8a	Machali	0–10	3.75	12.8	6.26	xxx	xxx	tr	zeo (x), ka (x), hmt/goeth (x), sm (tr)	tr		x	xx
8b		10–60	3.38	17.2	6.75	xxx	xx		zeo (x), sm (x), ka (x), hmt/goeth (x)	x			xxx
8c		60–120	5.66	4.8	5.92	xxx	xx		ka (x), zeo (xxx), sm (x), hmt/goeth (x)	xx			xx
T	Windblown tailings, Barahona		3.00	1.6	4.44	xxx	x	x	chl (x), hmt/goeth (tr)		xx	xxx	tr

am amphibole, chl chlorite, fsp feldspar, goeth goethite, hm hematite, ka kaolinite, Q quartz, sm smectite, sul sulfate, zeo zeolite, xxx major phase, xx phase clearly present, x minor phase, tr phase at trace level

Soil profiles were shovel dug, except for site 2 where an excavator was available. Samples were taken from a 10–15 cm layer of the top material depending on the depth of accumulated dried vegetation. The second composite sample was taken at a depth of 10 to approximately 70 cm (horizon free of underlying rock clasts) and the third sample from below that limit to 120 cm with the presence of underlying rock material. Additional samples at sites 1 and 2 responded to intercalations of tailings material (1b) and the presence of a reducing horizon (2c). For site 6, scarcely developed topsoil is followed directly by fractured rock. Samples were taken during in summer 2004 with maximum temperatures of 30°C and absence of rainfall, as access to several sites is difficult during rainy conditions or with snow cover.

Analytical methods

For all samples, grain size distribution was determined by wet sieving (ASTM mesh standards) and a Ro-tap orbital shaker SO1 from Bibby Stuart, GB. Prior to sieving, rocks and large roots were removed by hand.

Samples with more than 25% in weight, below 0.037 mm (400 ASTM mesh), were analyzed with a particle counter ELZONE 282 PC in the range of 80–3 μm . The weight percent of the <2 μm fraction was determined by centrifugation and evaporation at 60°C on a hotplate. This size fraction was chosen to match the clay size mineralogy analyzed. Chemical and mineralogical analyses were performed on the <2 mm fraction. Samples were milled in a tungsten carbide vibratory mill and if necessary re-milled by hand in an agate mortar.

The organic matter presence was determined by low temperature ashing using a Basic 200-G Plasma Processor at temperatures below 150°C. Sample pH was determined

after shaking a suspension of 10 g of the sample with 25 ml water for 1 h using a pH meter Horiba D-13.

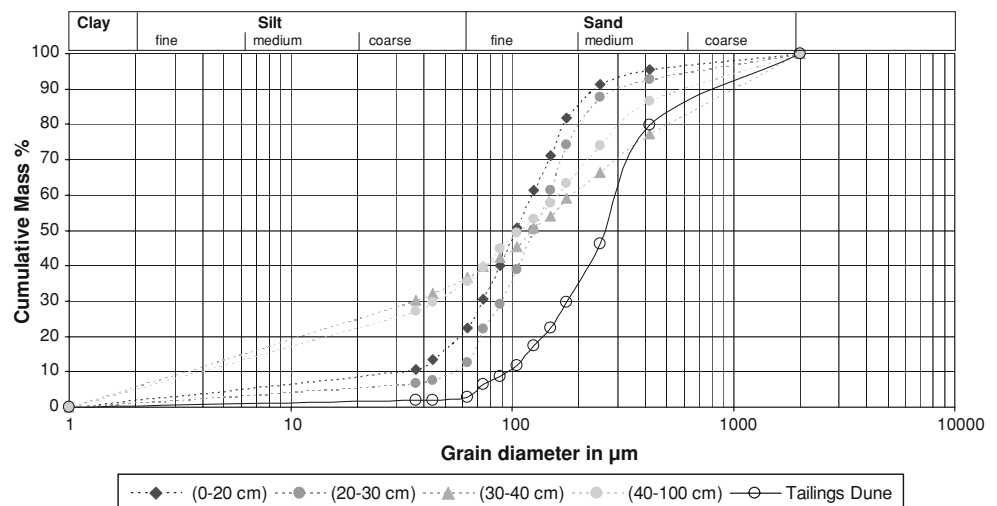
The mineralogy of whole rock and <2 μm clay size fractions was analyzed with a Rigaku Dmax C equipment using Ni-filtered Cu radiation. Major element analysis was carried out using a Rigaku System 3700 wavelength dispersive X-ray fluorescence spectrometer. As, Cu, Mo, Pb and Zn were determined by atomic absorption spectrometer using a Hitachi equipment, Model Z8100; hydride evolution improved the limit of detection of As. Turbimetric determination of S was carried out with a UV spectrometer, model U-100 Hitachi. To estimate the water-soluble and exchangeable fraction of the metals As and S, a modified partial sequential extraction following Hall et al. (1996) was employed. Samples were extracted independently with distilled water (5 g of sample in 20 ml) and a two-step sequence of 1M ammonium acetate (20 ml) at pH 7, followed by sodium acetate (20 ml) at pH 5. The separate water extraction was adopted to reduce analytical adjustment times for the AAS measurements. No sulfate was measured for the water extraction as mobilization was found to occur only in the sodium acetate step. A strong reference nitric acid leach was performed since at El Teniente, the elements of interest have only been reported from silicate phases as potentially adsorbed elements.

Results

Granulometric analyses

Soils from all sites and horizons have mixed grain sizes ranging from clay to sand fractions, where the <63 μm fraction may reach up to 40%. The cumulative grain size distribution curve (Fig. 3) of site 1 at the base of the

Fig. 3 Cumulative grain size distribution curves for site 1 and tailings material



Barahona dam demonstrates a clear influence of the windblown tailings material (Figs. 2, 3). Particle-counter-determined granulometry (80–3 μm) was found to be similar for all samples with a median at 9.6 μm . Figure 4 shows the relative proportions of clay, silt and sand size fractions for all samples, resulting in a cluster of sandy silty soils with minor (<20%) presence of clay size material. The weight percentage of the <2 μm fraction ranges from 1.6% for the windblown tailings, at the base of the Barahona dam, to 17% for sample 8b (Table 1).

Organic matter

The content of organic matter oscillates between 12 and 2.7% without observing any systematic decrease with depth in any of the sites. The highest organic matter contents is found in sample 2d (Table 1), a site exposed to permanent seepage at the base of the Barahona 1 dam, and site 4 (sample 4a, 10.16%) and site 3 (sample 3a, 9.66%) topsoils. Both sites are characterized by the presence of abundant dry shallow-rooted grass (sample 4a) and dead leaves (sample 3a).

Soil pH

The pH of soil solutions taken after several months without rainfall ranges from 3.5 to 6.8 (Table 1) and increases with depth for each site. Following the classification of Schachtschabel et al. (1979), El Teniente soils range from intensely acidic (pH range 3.9–3.0) to mildly acidic (pH range 6.0–6.9). Intensely to strongly acidic soils are found

at sites 1, 2 and 4 (Barahona dam and east of the impoundment).

Mineralogy

The dominant mineralogy in soil samples for all sites (Table 1) are quartz, plagioclase with a prevalence of intermediary compositions, minor K-feldspar, di- and tri-octahedral mica, goethite and hematite. Chlorite is found at sites 1, 2, 3 and 6; amphibole is present at sites 1, 2, 3 and 6. Halloysite is present in all soils except at site 6. Smectite is clearly detected in whole soil samples at sites 5, 7 and 8. At the latter two sites, zeolitization has affected the underlying rock as evidenced by the increasing presence of laumontite and heulandite at the base of both profiles. Phyllosilicates in the <2 μm fraction replicate the presence of the phyllosilicates found in the whole soil samples. Additionally, minor to trace levels of smectite are found for samples/sites 2a–c, 3, 4 and 8 a, b. Site 3 contains traces of a sulfate hydrate. The presence of this soluble phase is the result of strong evaporative conditions during the summer when the samples were taken. A more visible result of these climatic conditions is a temporary blanket of blue-green brownish efflorescences of bonattite ($\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$), chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and potassium aluminum sulfate ($\text{KAlSO}_4 \cdot 12\text{H}_2\text{O}$) at the base of the Barahona dams (Fig. 2).

Major elements

Major element composition of the soil samples is summarized in Fig. 7. For the Barahona sites 1, 2, 3 and 4, Al_2O_3 is enriched in the deeper profile samples, a similar observation holds for Fe_2O_3 , whereas SiO_2 shows the reverse trend.

Cation exchange capacity

The cation exchange capacity (CEC) comprises the Ca, Mg, K and Na available in charge compensating exchange positions *s. str.*, as well as cations adsorbed on mineral surfaces or available in gels and easily mobilized by ammonium acetate solutions. Ca is the dominant cation (Fig. 8), followed by Mg, K and Na at negligible levels. For all sites, except sites 6 and 7, the total cation exchange capacity ($\Sigma \text{Ca} + \text{Mg} + \text{K} + \text{Na}$) increases with profile depth.

Minor and trace element composition

The highest nitric acid extracted copper levels are found in topsoils for sites 1–6 (Fig. 9), all exceeding 1,000 mg/kg. A maximum of 2,265 mg/kg was detected in sample 1c

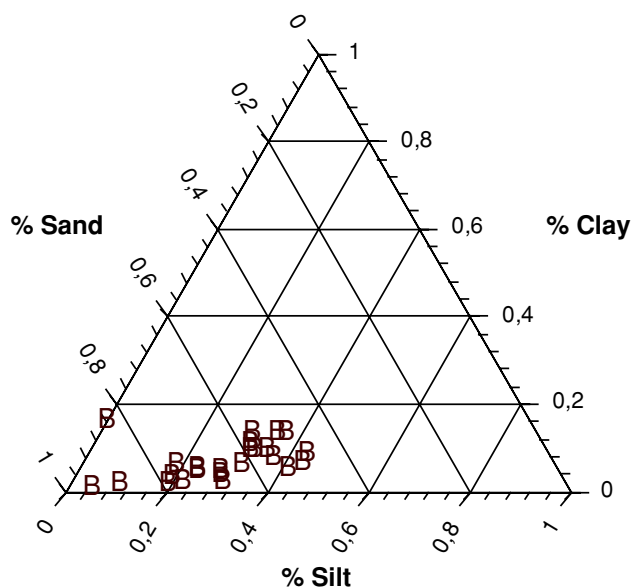


Fig. 4 Relative proportions of clay, silt and sand size material for all samples

located immediately below an interlayer of tailings sediment with 915 mg/kg Cu. The wind-transported tailings sediment (T) contains 287 mg/kg Cu.

Sulfate also is enriched in topsoils for sites 1, 3, 4, 5 and 6. At site 2, SO_4^{2-} levels exceed 4,000 mg/kg for all samples, reaching a maximum of 9,800 mg/kg in sample 2c. This site was the only one to display reducing conditions at medium depth (sample “c”). This site released a strong smell of rotten eggs when opened by the excavator and is permanently saturated with seepage water from the Barahona 1 tailings impoundment.

Nitric acid-extracted Pb levels remain below 26 mg/kg for all sites, except site 6 where 184 mg/kg was measured in the topsoil and 316 mg/kg in the underlying sample. The same feature applies to Zn, where the maximum values of 271 mg/kg and 439 mg/kg were detected in samples 6a and 6b, respectively.

Molybdenum shows clear enrichment in the topsoils for sites 1, 2, 3 and 6. This element is slightly enriched at the profile base for site 5, where smectite contents are high. Molybdenum is highest for the tailings sediment with 179 ppm.

The highest As concentrations have been found in samples 2d (285 mg/kg), 5c (207 mg/kg) and 6a (207 mg/kg). The tailings sediment (T) with 52 mg/kg has levels comparable to other sites or samples influenced by tailings material (e.g., site 1) as well as sample 6b.

Water extraction (Fig. 9) mobilized only <10 mg/kg Cu from the topsoils of sites 1–6. Sites 7 and 8 remained below the detection limit. Only Cu and Zn responded to ammonium acetate extraction for sites 1–6 following roughly the trend outlined by the HNO_3 -attacked sample. At pH 5, sodium acetate mobilized up to 80% of total SO_4^{2-} (4,480 mg/kg, site 2) and up to 50% of Cu (664 mg/kg, site 2). For Zn, a maximum of 10 mg/kg was obtained for

sample 2c and a maximum of 3.1 mg/kg As was mobilized. Lead exceeded the detection limit in only one sample (4a), whereas Mo was not detected in the extractions.

Discussion

To be able to clearly attribute the presence or the increase of trace elements in the soil to mining-related activities, regional and local background values should be analyzed before establishing comparisons with world average values (Smith and Hyck 1999). In the case of porphyry copper deposits, large-scale alteration halos and sub-economic copper mineralization can lead to large fluctuations in trace element concentrations of background rock. Furthermore, since the intrinsic focus of the mining industry lies in mineralized rock, they often discard research grade analysis of non-mineralized rock at an early stage (except when systematic sampling is carried out under an environmental perspective), unintentionally reducing the availability of useful information required to establish a regional background level of trace elements. Additionally, funding possibilities are scarce or absent for independent large-scale environmental background studies. For ET, the available trace element levels suitable as background data are summarized in Table 2 (Gramusset 2003; Cares 2004). Scarce data from agricultural soils of the Central Valley in the VI administrative region (Ahumada et al. 2004) also point to road traffic and pesticide use as an additional local source of trace elements in soils. For the regional soil sites, the influence of past emissions from the Caletones smelter cannot be completely excluded since SO_2 saturation zones were only delimited in the early 1990s, after more than 70 years of smelter operation. The extreme range of trace elements in the soil has been shown by Shacklette and

Table 2 Available reference background information for Cu, Mo, Zn, Pb, As and SO_4^{2-}

Author	Cu (mg/kg)	Mo (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	As (mg/kg)	SO_4 (mg/kg)	Observations
Cares (2004)	16–1340	3–76	36–511	6–56	6–25	n.a.	Intrusives and volcanoclastic rocks of Farellones Formation (La Huifa)
Gramusset (2003)	423	7	190	50	78	n.a.	
Ahumada et al. (2004) (1)	200–364	n.a.	n.a.	34–38	33–40	n.a.	Agricultural soils of Central Valley, Carretera del Cobre
Ahumada et al. (2004) (2)	442–947	n.a.	n.a.	25–37	33–34	n.a.	Agricultural soil of Central Valley, Panamericana highway
Ahumada et al. (2004) (3)	139–217	n.a.	n.a.	20–40	67–75	n.a.	Agricultural soil of Central Valley, Graneros village
Smith and Huyck (1999) (1)	14–100	1–15	40–200	12–20	1.7–5	260–1,200	Worldwide crustal abundance
Smith and Huyck (1999)	<1–700	<3–15	<5–2,900	<10–300	<1–8.8	<800–3,100	Concentration range of soils from the eastern US

Boerngen (1984) in Smith and Huyck (1999) for the eastern USA, demonstrating the clear need to establish local background values. To obtain realistic pre-mining baseline values (Plumlee 1999), soils without active agricultural use that have not been influenced by mining (including small-scale mining in adjacent valleys) need to be identified. This is not an easy task for the ET sector and the wider, geologically comparable surrounding region adjacent to the Coya valley. In the case of the Central Valley, longstanding intensive agricultural use precludes the availability of sites without human influence.

Despite the aforementioned drawbacks, the following points should be considered based on the results presented above.

Major element analyses corroborate material transport from the surface of the Barahona tailings impoundment (Fig. 1). The vicinity of the mica-rich tailings (preferentially wind transported mineral phases) would account for the near surface increase in K_2O levels, which is also reflected in soil mineralogy (sites 1, 2; Fig. 5), where mica derived from tailings is an important phase in the topmost soil horizons and display similar XRD spectra as the tailings material. The windblown tailings (T) show a composition similar to samples 1a, 1b and 2a, all influenced by the presence of tailings sediment. The increase of Al_2O_3 in deeper profile levels at sites 1–3 is considered to be due to the presence of kaolinite. The zeolitic laumontite and heulandite bearing sites 7 and 8 present a different major element pattern. CaO increases with depth, in agreement with the presence of calcic plagioclase and zeolites, where Ca predominates as charge compensation (Fig. 8).

The observed increase of CEC with profile depth is most noticeable for sites 2 (50 cmol/kg) and 5 (77 cmol/kg), where deeper soil horizons contain abundant smectite (Table 1) as well as high weight percentages of the $<2 \mu m$

fraction. The tailings sediment (T) and the soil strongly influenced by this windblown material (e.g., samples 1a, b), as well as site 6, have total CEC <2 cmol/kg, concordant with the absence of smectite. The highest CEC in topsoils (25 cmol/kg) are found for sites 7 and 8 with zeolites and no “mineral degeneration” (see below). For sites 7 and 8, CEC increases with depth due to the presence of zeolites in the soil and underlying rock.

Evidence of past SO_2 emissions on topsoils can be found in their decreased pH, a notorious feature for sites downwind from the Caletones smelter (sites 1–6). Increased topsoil acidity (even if seasonal) also results in the degeneration of smectite crystallinity, where this mineral is present. Figure 6 contrasts the $<2 \mu m$ size fraction XRD patterns for sites 5 and 7. At both sites, the intensity of the basal smectite reflection decreases notoriously. The partial dissolution of various smectite species in short-term leaching experiments has been demonstrated by Kelm and Helle (2003), and has been implied by head and tailings comparison in long-term leach operations (Domić 2001). The feature observed in Fig. 6 suggests that a long-term (80 years), mild and seasonal acid attack could have led to a partial dissolution of the smectite in the topsoil. The deterioration of phyllosilicate lattices under mild acid weathering conditions has been summarized by Nagy (1995 and literature cited therein). Furthermore, sulfate concentration is highest in topsoils, although S enrichment can occur in local anoxic conditions (Walton-Day 1999) by incorporation of S in organic species and sulfide precipitation, which could partially affect sample 2c, although in this case any sulfide phase remained below the detection limit of XRD. Arsenic emissions by the smelter have been a cause of concern for the ET sector in the past (<http://www.sustentable.cl>). However, As in topsoils for the foothills area does not clearly exceed the available background levels reported by Gramusset (2003; Table 2).

Fig. 5 Whole rock XRD traces for samples of sites 1 and 2.

Dotted box and black-rimmed boxes below $10^\circ 2\theta$: Basal chlorite and mica reflections in samples “a” and “b” “mimic” the tailings (T) traces; the same feature is observed for the remaining XRD traces, e.g., boxes at 13 and $20^\circ 2\theta$

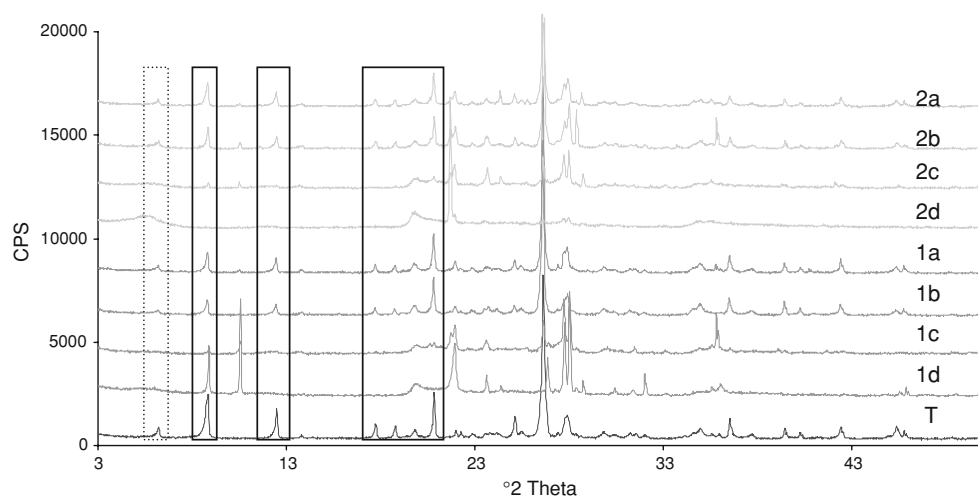
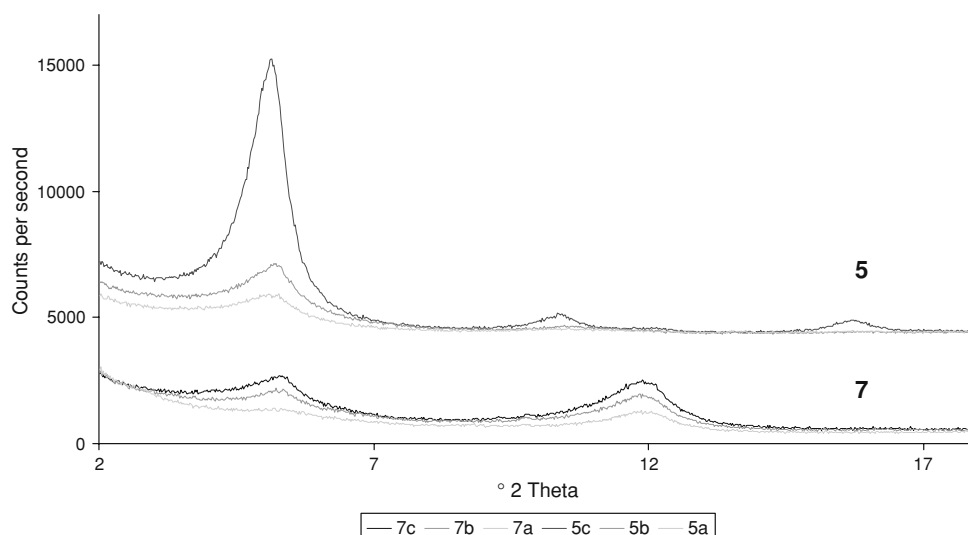


Fig. 6 Ethylene glycol saturated XRD traces of oriented mounts of samples from sites 5 and 7. Note the decrease in the intensity of the smectite reflection at 5° 2Theta from the *top* to the *base* of a soil profile



Only site 6 from the Andean mountains was notable with a record-setting As level of 225 mg/kg in the upper 10 cm, decreasing to 46 mg/kg in the underlying sample. This site shows absence of vegetation, although shallow roots are an indication of the presence of vegetation in the past. The loose top 10 cm are followed by intensely fractured base rock. The Andean climate and steep valley morphology further contribute to any surface accumulation of As (as well as SO_4^{2-} and Cu). For the foothills' soils, As is only enriched locally, such as in sample 2d and 5c, both horizons with presence of abundant smectite and potential to form a hydraulic barrier. Sample 2d is located underneath the only reducing horizon observed in this study. Here, reductive desorption in the overlying horizon (2c) could have contributed to As accumulation in the underlying (2d) horizon (Parker and Rae 1998).

Topsoils or horizons under direct influence of tailings sediment present the highest Cu accumulation. Although in this study, field observations, XRD mineralogy and grain size distribution (Table 1, Fig. 4) have confirmed the presence of tailings sediment in the top soils of sites 1, 2 and 3, the input of Cu through particulate matter emitted in the past from the Caletones smelter cannot to be ruled out, since Cu, As, Zn and Pb volatilize in furnaces and adhere to ash particles (Kelin et al. 1975, in Smith and Huyck 1999), although this process depends as much on the smelter feed as on the smelter technology used. Site 6 again differs from the foothills' samples (Cu 1,058 mg/kg in the topsoil, 789 mg/kg in the underlying sample). This site is located closest to the mineralized El Teniente complex with possible Cu levels above 1,000 mg/kg in the background rock.

Seepage from underneath the Barahona 1 tailings dam has added Cu to sites 1 and 2. Efflorescences of Cu sulfates hydrates are a clear evidence of this input, described in detail by Jambor et al. (2000; Figs. 7, 8)

The presence of Mo appears to be bound to the presence of tailing sediments in the upper soil horizons (sites 1–3), which is to be expected for tailings accumulated before the Mo recovery became economically relevant for Chilean porphyry copper ore. The tailings sediment (T) registered the highest nitric acid-extracted Mo value with 179 mg/kg. For the remaining sites, Mo levels should be considered within the range of the background rock (Smith and Huyck 1999).

High Zn mobility in the pH levels of the sampled soils does not allow the observation of any preferential enrichment. Lead concentration is highest at site 6 (sample 6b), suggesting that further sampling of the background rock is needed in the upper Coya Valley to obtain a clearer picture of background trace element ranges.

The nitric acid extraction levels for all elements at sites 7 and 8 are at least one order of magnitude below the levels of sites 1–6, leaving Mo already below the detection limit of 0.09 mg/kg (Fig. 9). Neither Cu nor SO_4^{2-} levels exceed 100 mg/kg, nor do the profiles present any marked enrichment or depletion tendency pointing to an influence of airborne contamination detectable with the methods and detection limits applied here. Furthermore, As, Pb and Zn levels are within the range reported for rocks from the Coya Machalí Formation (Gramusset 2003).

Water, ammonium acetate and sodium acetate extractions were selected to demonstrate potential mobilization under natural environmental conditions (rain, melting of snow) taking into consideration that measures have been taken to minimize the SO_2 output of the smelter and sulfuric acid aerosol dispersion. The mobilization of Cu (and to a lesser extent Zn) is possible at pH 7 in the presence of a suitable exchange cation. Release was more intense at pH 5 (sodium acetate), mobilizing up to 80% of SO_4^{2-} and 50% of Cu. This result underlines the concern not only for

Fig. 7 Major element distribution within the eight soil sites and composition of the tailings material (*T*)

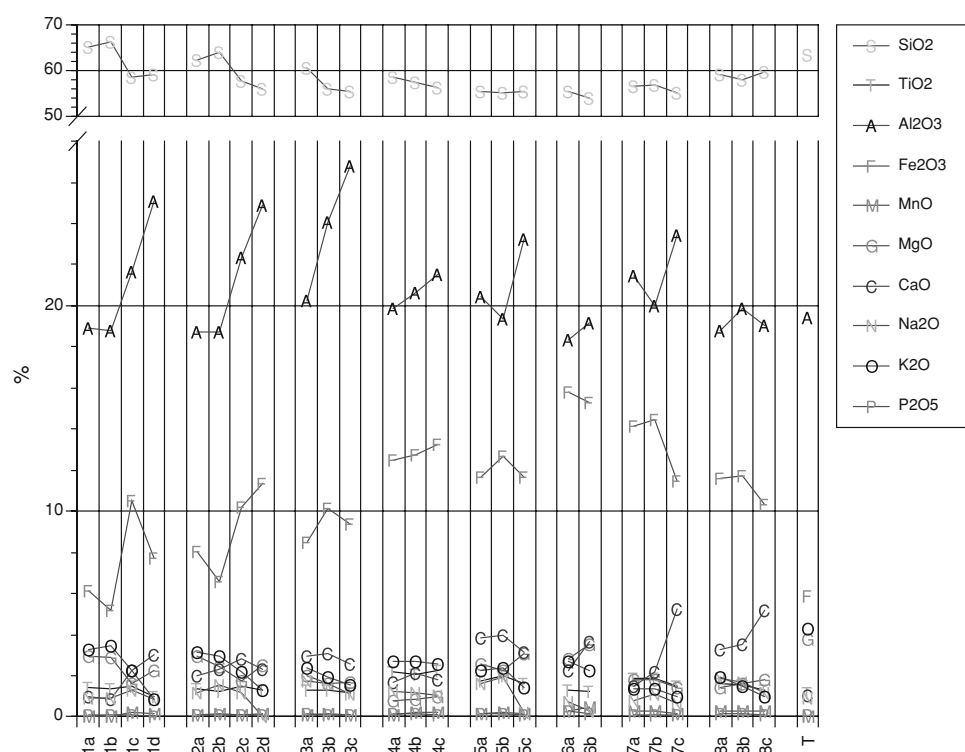
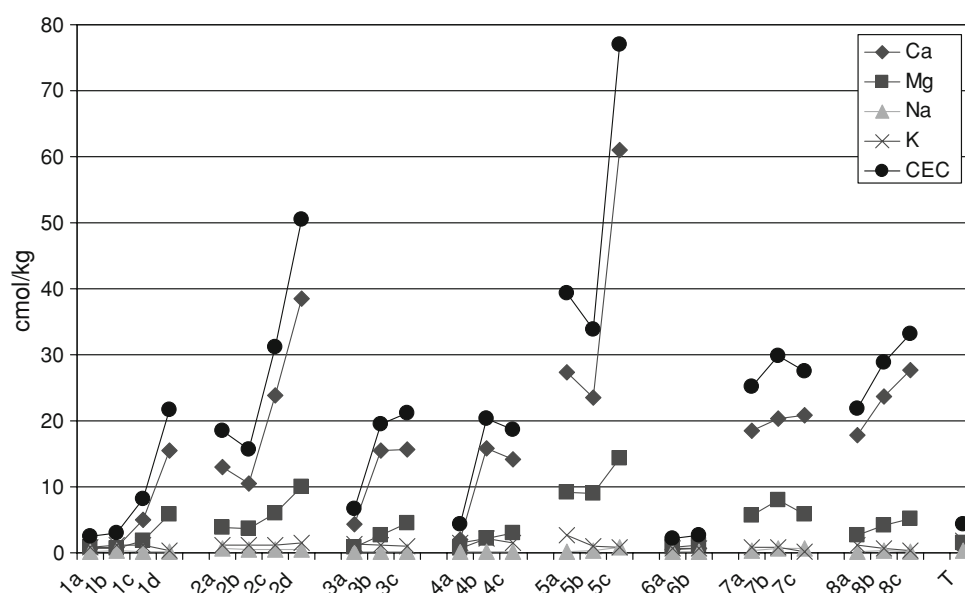


Fig. 8 Variation of the cation exchange capacity for the eight soil sites and the tailings material of Ca, Mg, Na, K and the sum of these elements (CEC)



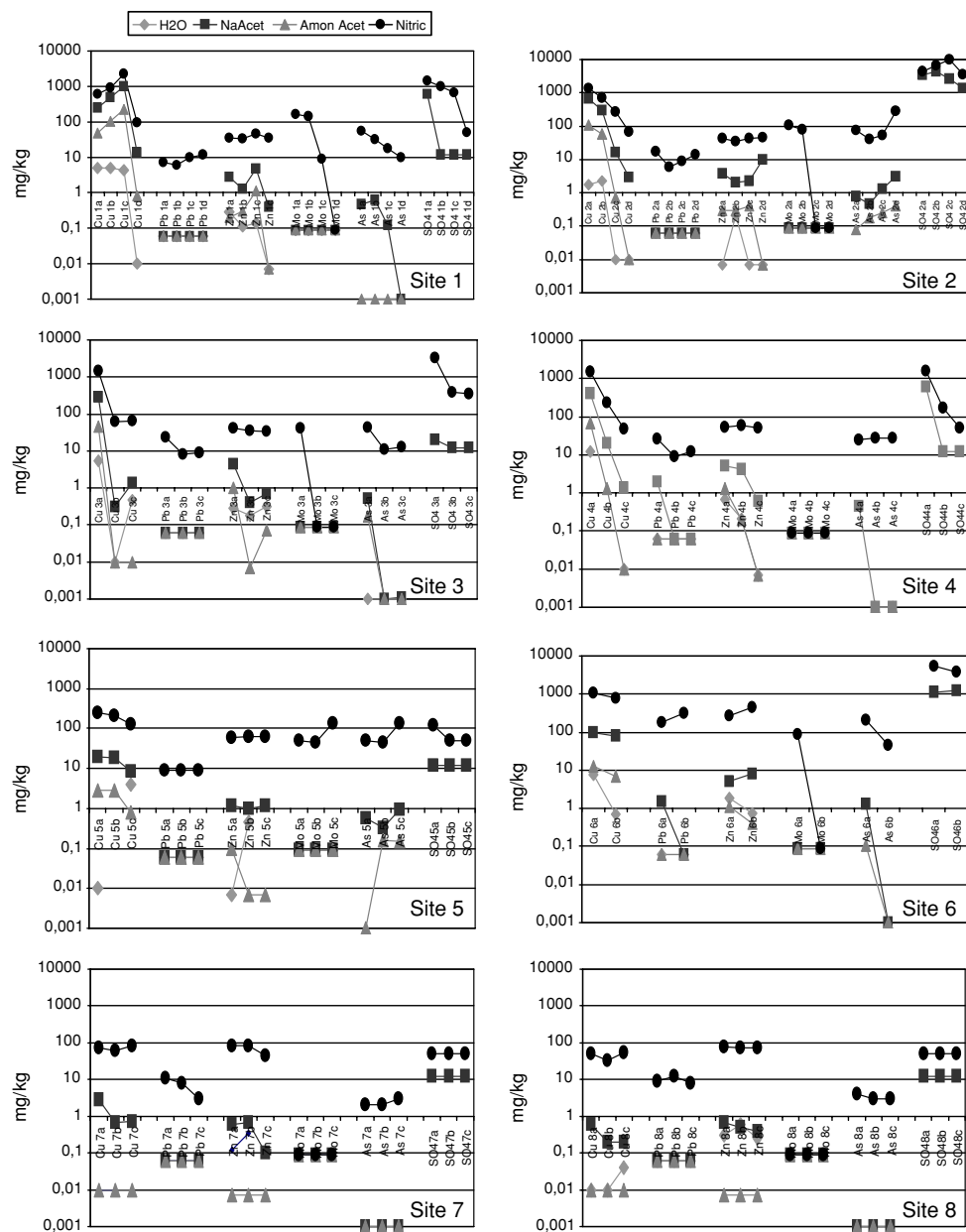
the easy Cu availability in soils, but also about its potential entry into the waterways, surpassing the established legal concentration limit for irrigation water.

Conclusions

The evaluation of the effect of past SO_2 , As and metal emissions from the Caletones smelter on eight soil sites,

with three of these sites under additional influence of seepage and windblown material from the Barahona 1 tailings dam, demonstrates Cu and SO_4^{2-} enrichment in the topsoils from locations downwind of the smelter; both elements are released partially by ammonium and sodium acetate extractions. Scarce background trace element data hinders the assessment of Mo, Zn, Pb and As concentrations in soils for the ET region. Here systematic subsurface sampling of the formations cropping out in the wider ET

Fig. 9 Minor and trace element distribution for the eight soil sites following water, sodium acetate, ammonium acetate and nitric acid extractions



compound is desirable to build up a background trace element information database. In soils, As concentrates in horizons with high smectite and/or organic matter contents. Windblown tailings material seems to be the source for Mo accumulation in topsoils. The detection limits of the AAS technique were not sufficient to evaluate a mild extractability of Mo, Zn, As and Pb, and another technique with improved detection limits is required.

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