

Monitoring of copper, arsenic and antimony levels in agricultural soils impacted and non-impacted by mining activities, from three regions in Chile

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This paper reports a comparative study of the concentration of three important environmental elements that are often found together in mineral deposits and then associated with mining activities; copper, arsenic and antimony. These elements were determined in 26 different agricultural soils from regions I, II and V in Chile, zones where the most important and biggest copper industries of this country are located. As background levels of these elements in soils have not been well established, in this study, both, impacted and non-impacted agricultural soils from different regions were considered. The relationships between the concentrations of these elements in soils were also examined. The concentration ranges for copper, arsenic and antimony were 11–530; 2.7–202 and 0.42–11 mg kg⁻¹ respectively. The copper concentrations in non-polluted soils from the north and central zone of Chile were similar. However, three sites from the north region have copper concentration as higher as 100 mg kg⁻¹, values that exceed the critical concentration for copper in soils. The concentration of arsenic and antimony in the north soils were higher than in non-impacted ones and, in the case of arsenic, greatly exceeded the world average concentration reported for this element in soils. The highest arsenic and antimony concentrations were found in Calama and Quillagua soils, two different sites in the Loa valley. The arsenic/antimony concentration ratio was higher in Quillagua soil. The high concentrations of three elements determined in impacted soils from region V (Puchuncaví and Catemu valleys) clearly shows the impact produced in this zone by the industrial and mining activities developed in their proximities. At Puchuncaví valley a clear decrease was observed in copper, arsenic and antimony concentrations in soils on the function of the distance from the industrial complex "Las Ventanas", and all concentrations exceeded the reported critical values for this matrix. Instead at Catemu valley, only the copper concentration was higher than this value. Statistically significant correlation was found for Cu–Sb in all soils; more significant Cu–As, Cu–Sb and Sb–As correlations were evaluated for soils from Puchuncaví and Catemu valleys, corroborating that high concentrations of copper, arsenic and antimony in these soils coming from the same pollution sources, the copper industry and the thermoelectric power plant.

Introduction

Deposition of metal-rich mine tailing, metal smelting, leather tanning, electroplating, emissions from incineration and fossil fuel combustion, intensive agriculture and the addition of soil amendments such as fertilisers, sewage sludge and fly-ash are most of the human activities which contaminate soils systems with large amounts of toxic elements. The list of sites contaminated with toxic elements grows through the years, presenting a serious problem and danger to the environment.

Arsenic, and to lesser extent, antimony are important environmental pollutants commonly associated with the mining and smelting of copper, lead, zinc and tin. It is well established that the occurrence of arsenic and associated toxic elements in copper ores and its presence in most pyrites cause gross contamination of the environment, specially in the vicinity of smelters treating such ores.¹ Compounds of these elements volatilise during the smelter process; stack dust flue gases from the smelter operation have contaminated soils and plants to varying degrees depending on the distance of sample collection from the smelter.² They are transported in the atmosphere over long distances; around smelters considerable ground level emissions occur.³

These metalloids may also reach soils *via* emission from incineration and fossil fuel combustion, addition of soil amendments such as fertilizers, sewage sludge and fly ash and also as a result of natural processes, such as, rock weathering, soil runoff and volcanic activities. In the case of Chile, during the late Tertiary and the Quaternary, the Altiplano region (in the north of country) was affected by intense volcanic activity,^{4,5} the lava flows containing deposits of sulfides ores rich in arsenic compounds.

Numerous studies have been conducted demonstrating that high concentrations of arsenic are naturally present in the different compartments of the Chilean Altiplano ecosystem, with the consequently health risk.^{6–12} There is increasing scientific evidence linking the chronic arsenic exposure of this population to cancers of the skin, various internal cancers and also to some serious cardiovascular diseases.^{13–15}

Chile is an important mining country, with a great number of metallic and non-metallic deposit. The mining activity has been developed in the north-center of Chile from the "La Colonia" period (XVIII century), and the age of copper was begun in the XX century until today. The north region, in the Andes mountain, is the zone where the principal and biggest

mines of copper ores and one of the more important reserves of this element in the world are located. In the sulfide copper ores, beside arsenic, other toxic elements are present in significant amounts, *i.e.* antimony is generally associated with arsenic in sulfide ores.¹ In spite of the economical importance of mining activities in Chile, the mining of copper ores have produced some adverse effects on the environment, due to discharge of tailing wastes into rivers or sea, release of particulate material and gases into the atmosphere by the smelters, *etc.* However, little information has been published on the concentration of toxic elements in the environmental matrices or the degree of contamination caused by these activities, except for the available information on the distribution of arsenic in the Antofagasta region.^{9,10} There is even less information about the antimony concentration in all kinds of environmental matrices.

The environmental monitoring of antimony is of growing interest; it is a non-essential element that has chemical behavior and toxicity similar to those of arsenic.¹⁶ Each is acutely toxic to man and animals, and both elements have been shown to exhibit chronic toxic effects at very low intake rates.¹⁶ Antimony is listed by the United States Environmental Protection Agency as a priority pollutant. Usually concentrations of naturally occurring antimony in soils are in the range of 0.2 to 10 mg kg⁻¹ and are about 5–10% of those of arsenic.¹⁷ The environmental concentration of both metalloids differs in a broad range. In soils their concentrations can reach several hundred mg kg⁻¹, especially in polluted sites.¹ Moreover, recently it has been reported that simultaneous exposure to antimony and arsenic, can increase the arsenic toxicity.¹⁸

The determination of toxic elements in the Chilean environment are needed, in order to assess their toxicity, to assess long-term trends as well as to predict future trends. Moreover, there is no available information about the concentration of antimony in Chilean soil. The aim of this study was to determine and compare the concentrations of copper, arsenic and antimony (three elements that are often found together in minerals deposits) in agricultural soils from regions I, II and V in Chile, in zones where the most important and biggest copper industries are located. As background levels of these elements have not been well established, in this study, both impacted and non-impacted agricultural soils by mining activities from the different regions were considered. The relationships between the concentrations of these elements in soils were also examined.

Although many analytical methodologies are applied to determine arsenic and antimony in environmental samples, the most commonly used methods involve atomic spectrometry. For the past 10 years, the most widely used techniques to determine these metalloids have been hydride generation coupled to atomic absorption spectrometry (HG-AAS). Actually, the atomic fluorescence spectrometry coupled to hydride generation (HG-AFS) is an alternative atomic technique that can be used, with the advantage that its analytical performances are better. Authors using HG-AFS have reported lower detection limits and lesser interference than HG-AAS.^{19–21} In this study the determination of both metalloids was carried out by HG-AFS.

Materials and methods

Instrumentation

The determination of copper and iron in soils was performed by AAS. The pre-diluted sample solution was aspirated in the air acetylene flame of a model 905 GBC AA spectrophotometer, using the instrument and flame setting as recommended by the manufacturer.

For the HG-AFS antimony and arsenic determinations, a PSA Analytical Ltd. continuous flow system was used. The sample solution or 1.5% m/v HCl and 0.7% m/v NaBH₄ were

continuously pumped to the separator. The respective hydride was generated and purged with argon (300 mL min⁻¹), coupled *via* a commercial dryer membrane (Perma Pure product, dryer model MD-110-12 FP), to an atomic fluorescence spectrometer (PSA) (Orpington, Kent, UK) Millennium Excalibur model (10055), equipped with an antimony or an arsenic boosted discharged hollow cathode lamp (BDHCL). In this model the atomisation flame was sustained with H₂(g) obtained during the hydride generation reaction and flushed to the burner by argon flow.

Reagents

High quality water (18 MΩ) obtained from a Nanopure system (Barnstead) was used for to prepare all solutions. Stock solution of 1000 mg L⁻¹ Sb(III) was prepared dissolving solid antimony potassium tartrate K(SbO)C₄H₄O₆H₂O (Aldrich, 99.95% purity) in 1% m/v ascorbic acid (Merck); stock solution of 1000 mg L⁻¹ As(III) and Cu(II) were obtained from the respective standard solution Titrisol®, Merck. All standard solutions were stored at 4 °C in polyethylene bottles. Working solutions were prepared daily by an appropriate dilution, those of Sb(III) were diluted with 0.1% m/v ascorbic acid.

High purity nitric, hydrochloric, hydrofluoric and sulfuric acid (Suprapur®, Merck) were used for digestion of soils.

Sodium borohydride solution (0.7% m/v) was prepared dissolving NaBH₄ powder (Merck) in 0.4% m/v NaOH solution (Merck). This solution was prepared daily just before use or stored for up to three days at 4 °C.

All glassware and Teflon vessels were soaked in 10% v/v nitric acid for several days to leach trace elements, rinsed with deionised water and stored in closed plastic bags.

Sampling sites

In Fig. 1 and Table 1 are summarized the geographic situation in Chile of each site and the abbreviations used for the soil samples in the text. Three different geographical zones were considered for this study: Tarapacá, Antofagasta and Valparaíso Regions (I, II, and V region in Chile, respectively). These are some of the principal zones where mining activities are developed in this country. Soil samples were collected from sites where agricultural activities are developed. Tarapacá and Antofagasta regions are recognised as some of the most desert zones of the world, where rainfall is extremely scarce. Only in the Altiplano zone (in the Andes Mountains of these regions), rain and snow fall in the summer period (January and February); this phenomenon is called "the Bolivian winter". As water in this region is very scarce, the agricultural activities are developed in little valleys ("quebradas"), which are irrigated by streams, water spring or rivers. These quebradas are located on the "pre-cordillera zone" of the Andes Mountains. For this reason in region I, soils were sampled from "Quebrada de Tarapacá", "Quebrada de Parca", "Mamiña" (a site with a hot spring located at 3000 m), from "Oasis de Pica" (an oasis located at 120 km at the southeast of Iquique city, where natural water emerges from the earth) and from two non agricultural sites in the Altiplano region, "Huasco" and "Coposa" salt lakes, located at 3000 m altitude, at east of Iquique city. In region II, three different sites from the "Loa valley" were sampling: "Chiu-Chiu" (placed 35 km east of Chuquicamata, the biggest open copper mine in the world, where there is also a copper smelter and electrorefinery), Calama (16 km south of Chuquicamata) and Quillagua, a site placed down stream from Calama. Two non-agricultural soils were also sampled in this region, located around Antofagasta city.

In region V two zones impacted by mining activities were selected: Puchuncaví and Catemu valleys. The first one is an agricultural zone located 35 km north of Valparaíso city, impacted by the industrial complex "Las Ventanas" where

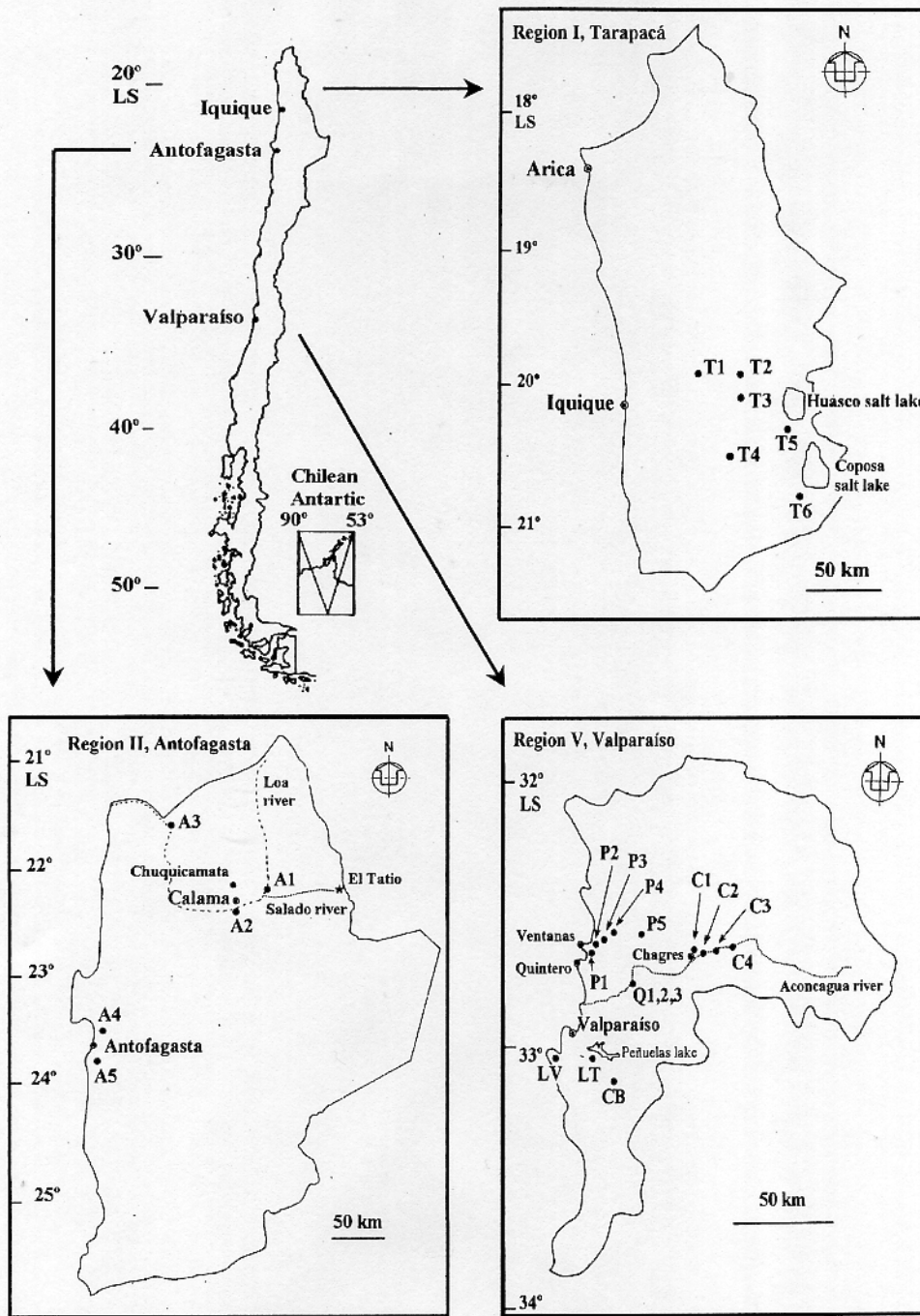


Fig. 1 Map of Tarapacá (I), Antofagasta (II) and Valparaíso (V) regions in Chile, showing the sampling sites.

there are both a smelter and electrorefinery plant of copper ore, as well as a coal fired thermoelectric plant. In this valley the soil samples were collected in five sites placed at different distances from the industrial complex: La Greda (2 km), Los Maitenes (2.6 km), Campiche (6 km), Puchuncaví (8 km) and Nogales (26 km). The other zone (Catemu valley) located at 75 km northeast from Valparaíso city, in the Aconcagua river valley, also receives the influence of a copper ore smelter (Chagres). In this area, the soils were collected in four sites placed at different distances east from the smelter: Catemu (4 km), San José (5.5 km), Santa Margarita (7 km) and Panquehue (13.5 km). The choice of sites in both impacted zones was made taking

into account the topography and the prevailing direction of winds²² and the distance from the sources.

Soil samples were also collected in three other sites in the Aconcagua valley, in the proximity of Quillota city, at 40 km northeast from Valparaíso city: Rautén, Quillota and Pocochay. It is important to remark that the Aconcagua valley is one of the most important agricultural zone in Chile, irrigated by the Aconcagua River, where all kind of comestible vegetables and fruits are cultivated. Finally, three sites non-specifically impacted by mining activities in the region of Valparaíso were chosen for soils collection. Laguna Verde, Las Tablas and Casablanca, at 7 km south, 15 and 40 km southeast

Table 1 Geographic situation of sites and distances from copper smelter where soils were collected

Geographic situation in Chile	Site	Distance from the source/km	Sample abbreviation
Region I (Tarapacá)	Quebrada de Tarapacá	—	T1
	Quebrada de Parca	—	T2
	Mamiña	5 (E)	T3
	Pica	—	T4
	Huasco	—	T5
	Coposa	—	T6
Region II (Antofagasta)	Chiu-Chiu	35 (E)	A1
	Calama	16 (S)	A2
	Quillagua	—	A3
	Antofagasta Norte	—	A4
	Antofagasta Sur	—	A5
Region V (Valparaíso)	La Greda	2 (E)	P1
	Maitenes	2.6 (E)	P2
	Campiche	6 (E)	P3
Puchuncaví Valley	Puchuncaví	8 (E)	P4
	Nogales	26 (E)	P5
Catemu Valley	Catemu	4 (E)	C1
	San José	5.5 (E)	C2
	Santa Margarita	7 (E)	C3
	Panquehue	13.5 (E)	C4
Near to Quillota city	Rautén	—	Q1
	Quillota	—	Q2
	Pocochay	—	Q3
Casablanca Valley	Casablanca	—	CB
Near to Peñuelas lake South Valparaíso	Las Tablas	—	LT
	Laguna Verde	—	LV

from Valparaíso city, respectively. Las Tablas is placed in the vicinity of one lake that is used as a freshwater pool for region V. Casablanca is an agricultural valley with important vineyard planting. This location has been often selected as a reference area in environmental problems associated with the industrial complex "Las Ventanas", due to its similar characteristics with Puchuncaví valley.^{23,24} Summarizing, in this work 26 different soils were collected from three different regions in Chile.

Soil collection and treatment

The soil samples were taken to a depth of 0 to 20 cm. Approximately 5 kg of soils were collected from each site (composite samples from different points, from approximately 1 hectare) and were placed in plastic bags. Soils were air dried and sieved to 2 mm. The <2 mm fractions were stored in polyethylene bottles in a desiccator until analysis. The concentration of iron and some characteristics of the sampled soils were determined. The concentration of Fe was determined by FAAS. The pH values of soils were measured using a 1:2 suspension (soil weight: water volume); the *p_e* values were calculated from the potentials measured in the same solutions, using Pt and calomel electrodes. Organic matter (OM) was determined by dichromate oxidation followed by the titration of excess dichromate with Fe(II).

Digestion of soils

The digestion of soil samples or certified reference soils was performed in a microwave oven operating system, (Microdigest A300, Prolabo) or in a high pressure PTFE vessel, at 170 °C, using HNO₃-HCl-HF acids mixture. 1.0 g of dry soil (<2 mm) was weighed accurately (in triplicate) into a PTFE vessel, 6 mL of concentrated HNO₃ were added and then allowed to stand overnight at room temperature. The samples were then digested using an optimized microwave program, adding 8 mL of HCl and 10 mL of HF. After cooling, the digested samples were quantitatively filtered and diluted to 50 mL with

deionised water. The optimization and detailed digestion procedure employed was previously described.²⁵

Determination of Cu, As and Sb in soils

Copper in the digested solutions from soils was determined by flame atomic absorption spectrometry (FAAS), by a simple calibration mode, measuring the absorbance signal at 324.7 nm and using a hollow cathode lamp as excitation source operated at 3 mA.

Total antimony and arsenic determinations by hydride generation requires antimony and arsenic to be present in the (III) oxidation state for optimum production of the respective hydride (SbH₃ and AsH₃). As Sb(V) and As(V) were the species present in the digested soil solutions, pre-chemical reductions of Sb(V) to Sb(III) and As(V) to As(III) in soils solutions were performed by KI/ascorbic acid, before the hydride generation. The procedure employed to determine total antimony in the digested solutions from soils and CRM materials was previously described.²⁵ Briefly, an aliquot of variable volume 0.2–1.0 mL (depending of the Sb concentration) was mixed with 2.5 mL of KI (15% m/v) + ascorbic acid (3% m/v) + 3 mL of concentrated HCl. This solution was then heated in a microwave oven, for 3 min, at 120 W or in a water bath at 90 °C, for 40 min. The cooled solution was finally diluted to 25.0 mL, with deionised water. To determine total arsenic 0.05–0.2 mL of sample was placed into a volumetric flask, then 5 mL of 15% m/v KI + 3% m/v ascorbic acid + 6 mL of concentrated HCl were added, the solutions was allowed to stand for 30 min, at room temperature and then made up to 50 mL with deionised water. The sample solution was then pumped into the flow system and the respective hydride was generated. The determination of antimony and arsenic were performed by a simple calibration mode, since no matrix effect was detected in the determination of both metalloids. The parameters used to determine antimony and arsenic in soils by HG-AFS are summarized in Table 2. The accuracy of the methodologies employed were assessed analyzing two certified reference soils from NIST: San Joaquin and Montana soil (SRM 2709 and 2710, respectively).

Table 2 Operating conditions employed to determine arsenic and antimony in soils by HG-AFS, (atomic fluorescence spectrometer PS Analytical, Excalibur Millennium Model)

Parameter	Condition		
	As		Sb
BDHCL	Primary	27.5	17.5
Intensities/mA	Boosted	35	15
Concentrations	HCl NaBH ₄		1.5 M 0.7% (m/v) in 0.4% (m/v) NaOH
Flow rates/ml min ⁻¹	HCl NaBH ₄ Sample Carrier gas/Ar Drier gas/N ₂		9 4.5 9 300 2500
Pre-reduction step	Experimental conditions	1.5% (m/v) KI + 0.6% (m/v) ascorbic acid in 1.5 M HCl, room temperature, 30 min.	1.5% (m/v) KI + 0.6% (m/v), ascorbic acid in 1.5 M HCl, 90 °C in a water bath, 40 min.
Calibration curve	Concentration range/ $\mu\text{g L}^{-1}$	0.05–0.800	0.050–0.800
	Sensitivity UF ^a /L μg^{-1}	1038	1318
	Detection limit ^b / $\mu\text{g L}^{-1}$	0.020	0.010
	Detection limit ^c / $\mu\text{g kg}^{-1}$	100	50
	Precision ^d for 0.5 $\mu\text{g L}^{-1}$	2.0%	2.4%

^aUF = Units of fluorescence. ^bLOD = 3 SD/*m*, SD = standard deviation of 10 measures of the blank solutions, *m* = slope of the calibration curve. ^cLOD in the experimental conditions employed. ^dExpressed in terms of variation coefficient for *n* = 6.

Table 3 Certified and experimental copper, arsenic and antimony concentrations in certified reference materials

CRM	Element	Certified value/mg kg ⁻¹	Experimental value/mg kg ⁻¹
San Joaquin soil NIST 2709	Cu	34.6 ± 0.7	31 ± 3
	As	17.7 ± 0.8	17.2 ± 0.6
	Sb	7.9 ± 0.6	7.6 ± 0.7
Montana soil NIST 2710	Cu	2950 ± 130	2812 ± 42
	As	626 ± 38	593 ± 10
	Sb	38.4 ± 3	34 ± 2

Results and discussion

Quality control

Determination of trace elements in environmental samples requires strict quality control of the analysis. For this purpose it is necessary to carry out the analysis of certified reference materials (CRM) that match as closed as possible the matrix type and the element concentration level of the real samples. In this work the accuracy of the analytical methodologies employed for the determination of Cu, As and Sb in soils were assessed analyzing two certified reference soils from NIST: San Joaquin soil and Montana soil (SRM 2709 and 2710, respectively). As can be seen in Table 3, the values determined for Cu, As and Sb in both CRM are in agreement with the certified values. The measured values, including their uncertainties (standard deviation) lie within the certified values and their uncertainties, and therefore there are no reasons to believe that the differences are significant.²⁶ Contamination was not observed during the whole procedure, not any of the three elements determined was detected in the blank samples.

Some chemical characteristics of soil samples

As can be seen in Table 4, with the exception of La Greda, Rauten, Laguna Verde and Las Tablas soils, all pH values determined in soil samples were above 7. Then, according to the Blakemore classification²⁷ all soils are neutral or slightly alkaline. The lowest pH values were determined in La Greda soil (6.72), probably due to its proximity to the industrial complex Las Ventanas; and in Laguna Verde (5.77), site located near a thermoelectric power plant. The pH values in soil collected from regions I and II were higher than in soil from region V and similar to those described as "normal" for semi arid regions.²⁸ This fact is due to the carbonate levels present

in arid soils from north of Chile.²⁹ On the other hand, the *p*_e values in soils were between 6.39 and 10.06, which permitted the classification of these soils as "oxic". Oxic conditions usually give values on the *p*_e range 5.1–13.5, but mostly from

Table 4 Some chemical characteristics of the sampled soils from different regions in Chile

Site	pH	<i>p</i> _e	Organic matter (%)	Fe (%)
T1	8.71 ± 0.01	8.94	0.80 ± 0.01	2.1 ± 0.1
T2	8.35 ± 0.06	9.26	1.63 ± 0.01	2.5 ± 0.1
T3	7.73 ± 0.02	9.13	1.63 ± 0.04	2.5 ± 0.2
T4	8.90 ± 0.04	8.54	2.8 ± 0.2	2.6 ± 0.3
T5	9.80 ± 0.10	6.39	0.44 ± 0.01	0.9 ± 0.1
T6	7.60 ± 0.02	6.10	0.15 ± 0.01	2.2 ± 0.1
A1	8.76 ± 0.07	8.28	1.62 ± 0.02	1.9 ± 0.1
A2	8.96 ± 0.05	9.01	1.16 ± 0.02	1.4 ± 0.1
A3	8.39 ± 0.01	9.74	2.96 ± 0.01	1.8 ± 0.1
A4	7.5 ± 0.1	9.18	0.08 ± 0.01	2.7 ± 0.3
A5	8.0 ± 0.1	10.38	<0.02	2.5 ± 0.3
P1	6.72 ± 0.01	9.28	1.22 ± 0.09	3.7 ± 0.1
P2	7.35 ± 0.03	8.96	1.46 ± 0.06	4.7 ± 0.1
P3	7.86 ± 0.03	9.38	0.92 ± 0.02	4.0 ± 0.2
P4	7.29 ± 0.01	8.99	3.0 ± 0.1	3.8 ± 0.1
P5	7.26 ± 0.01	9.08	2.58 ± 0.03	4.1 ± 0.1
C1	7.31 ± 0.02	8.92	3.1 ± 0.2	5.4 ± 0.1
C2	8.04 ± 0.03	8.28	1.56 ± 0.04	4.2 ± 0.1
C3	7.84 ± 0.07	8.64	2.25 ± 0.06	3.2 ± 0.2
C4	8.09 ± 0.01	8.45	2.03 ± 0.04	4.3 ± 0.2
Q1	6.85 ± 0.09	8.40	2.55 ± 0.08	6.0 ± 0.2
Q2	7.39 ± 0.08	8.15	1.99 ± 0.08	5.4 ± 0.2
Q3	7.2 ± 0.2	7.38	2.87 ± 0.06	5.4 ± 0.2
CB	7.79 ± 0.05	8.69	1.50 ± 0.01	3.6 ± 0.1
LT	6.87 ± 0.02	9.84	1.86 ± 0.05	3.7 ± 0.1
LV	5.77 ± 0.04	10.06	0.90 ± 0.01	1.7 ± 0.1

6.8 to 10.1.³⁰ The main feature that distinguishes soils from regolith (decomposed rock) is the presence of living organisms, organic debris and humus. In the sampled soils, the organic matter contents were lower than 5%, and were classified as mineral soils.³¹ The iron contents in soils (0.9–6.0%) were into the normal range described for this matrix,³¹ and the higher values were determined in soils collected in region V, which is probably due to the major evolution by weathering suffer by these soils than them of north region.

Copper, arsenic and antimony concentrations in agricultural soils

Cu, As and Sb concentrations in soils are presented in Table 5. As can be seen, a wide copper concentration range was determined in the soil samples, values were between 11 mg Cu kg⁻¹ (Huasco), and 530 mg Cu kg⁻¹ (La Greda). An overview, presented in Fig. 2, shows that the copper concentrations in soils from the north region were lower than in soil from valleys impacted by copper smelters, but were similar to those determined in soils collected in non impacted sites from Valparaíso region, *i.e.* Casablanca, Las Tablas, Laguna Verde (13.2–40 mg Cu kg⁻¹).

With the exception of Mamiña (T3), Chiu-Chiu (A1) and Antofagasta Norte (A4), the average copper concentration in north Chilean soils was 28 ± 12 mg kg⁻¹, this value is similar to the world average copper concentration in soils (30 mg kg⁻¹),³¹ and not any of these soils reached the reported critical toxicity range (60–125 mg kg⁻¹). The copper concentration in Mamiña and Chiu-Chiu soils was approximately 100 mg kg⁻¹. In Mamiña, the presence of geothermal springs with high sulfide concentrations, employed to irrigate the culture crops and alfalfa, must contain also high copper concentration. On the other hand, the copper mining activities developed in "El Colorado", located at approximately 5 km from this village, are also a source of this high copper concentration in Mamiña soil. Chiu-Chiu is another site affected by mining activities, this village is located in the proximity of Chuquicamata, the biggest copper mining in Chile; gaseous emissions and/or particulate material from this mine are transported by winds to this site. It is important to remark that due to this fact, in 2002 the population

Table 5 Copper, arsenic and antimony concentrations in soils (mg kg⁻¹) from different regions in Chile

Site	Cu	As	Sb
T1	31 ± 3	34 ± 2	1.8 ± 0.1
T2	26 ± 1	9 ± 1	1.2 ± 0.1
T3	100 ± 4	20 ± 3	2.4 ± 0.1
T4	14 ± 1	21 ± 1	4.2 ± 0.1
T5	11 ± 1	34.1 ± 0.4	2.4 ± 0.1
T6	37 ± 3	49 ± 1	3.3 ± 0.2
A1	108 ± 3	43 ± 1	0.6 ± 0.1
A2	46 ± 3	106 ± 5	11 ± 1
A3	35 ± 2	202 ± 8	11 ± 1
A4	240 ± 6	19 ± 1	2.3 ± 0.1
A5	25 ± 1	14.3 ± 0.3	3.4 ± 0.2
P1	530 ± 38	52 ± 2	6.7 ± 0.3
P2	282 ± 1	40 ± 1	6.6 ± 0.4
P3	329 ± 26	37 ± 1	5.5 ± 0.6
P4	255 ± 6	30 ± 2	5.7 ± 0.4
P5	104 ± 4	13.4 ± 0.5	1.8 ± 0.2
C1	140 ± 4	11.3 ± 0.5	4.1 ± 0.3
C2	179 ± 4	20 ± 1	4.1 ± 0.3
C3	233 ± 6	23 ± 1	3.6 ± 0.3
C4	75 ± 5	21 ± 1	3.7 ± 0.2
Q1	159 ± 12	24 ± 5	2.1 ± 0.1
Q2	81 ± 5	19 ± 1	1.8 ± 0.2
Q3	88 ± 1	49 ± 1	1.8 ± 0.1
CB	35 ± 1	3.6 ± 0.2	1.0 ± 0.2
LT	40 ± 1	4.7 ± 0.6	0.42 ± 0.04
LV	13.2 ± 0.2	2.7 ± 0.1	2.2 ± 0.2

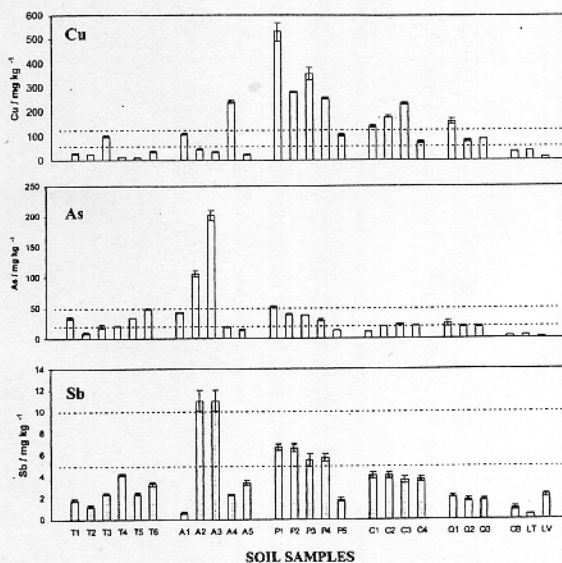


Fig. 2 Copper, arsenic and antimony concentrations in Chilean agricultural soils. The abbreviation of soil samples is detailed in Table 1. The dotted lines represent the critical concentration ranges in soils.

that lived in Chuquicamata town was moved to Calama city. On the other hand, we do not have any possible explanation about the high copper concentration determined in Antofagasta Norte soil, unless ore storage is located in the proximity of this site.

It is very clear that the copper concentration in soils from Puchuncaví and Catemu valley were higher than in non impacted soils from region V. The average copper concentrations for these contaminated soils were 305 mg kg⁻¹ and 157 mg kg⁻¹, respectively. This fact shows the impact produced by the industrial activities developed in both valleys, especially in Puchuncaví valley. As can be seen in Fig. 3A, in this valley a clear decrease was observed in copper concentration in soils as a function of the distance from Las Ventanas industrial complex: $\text{Cu (mg kg}^{-1}\text{)} = 683 \text{ distance}^{-0.53} \text{ (km)}$ ($R^2 = 0.8048$). Chiang *et al.* have reported a similar behavior for the copper and arsenic mass in airborne particulate material deposited as a function of the distance from the smelter, located at Las Ventanas, in Puchuncaví valley.³² Results of the copper concentration in soils corroborate that this contamination had been produced by atmospheric deposition of particulate material emitted by the industrial activities developed in this zone.

This behavior is not so clear at Catemu valley, where Santa Margarita soil (C3) has a copper concentration up to 1.7 times the level found at Catemu, the site nearest to smelter. (It is important to remark that the road crossing at Santa Margarita has been filled with solids wastes from Chagres smelter.) Summarizing, in Puchuncaví and Catemu valley the more impacted sites by copper are La Greda and Santa Margarita, respectively. Moreover, excluding the more distant sites from copper smelters in both valleys (*i.e.* Nogales and Panquehue at Puchuncaví and Catemu valleys, respectively) the copper concentration in all these soils exceeded the reported critical toxicity range values.³¹

On the other hand, the copper concentration in soils collected in the vicinity of Quillota city (samples Q1 to Q3) were higher than those obtained in other non-impacted sites in the same region; Rauten (Q1) has a copper concentration as higher as 150 mg kg⁻¹. This fact can be associated with the use of fungicide sprays (containing this element) on orchards, since it has been reported that high copper concentration in agricultural soils can be due to periodic fumigation with this kind of product.³¹ However, it is also possible that this contamination

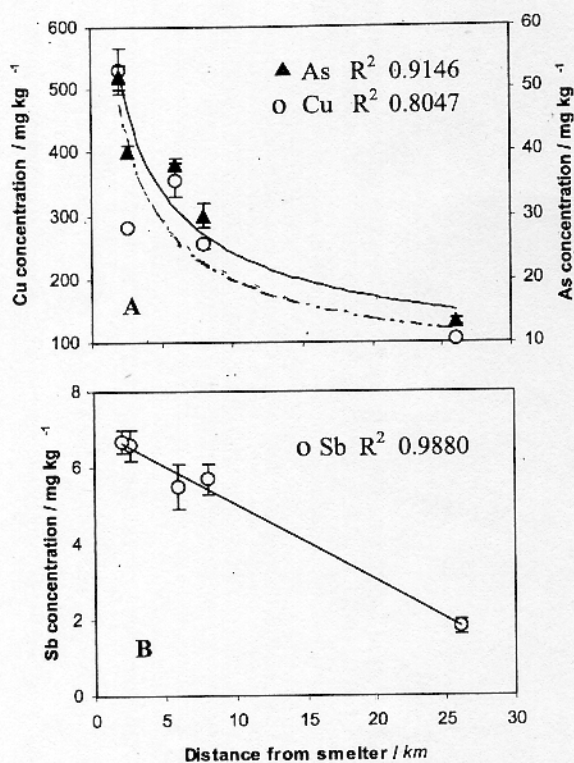


Fig. 3 Relationships between the element concentration in soil from Puchuncaví valley, and the distance from Las Ventanas industrial complex. (A) Copper (O) and arsenic (▲) (B) antimony.

was produced by irrigation of these soils with Aconcagua river water, contaminated with this element by the mining activities developed in a copper mine, located in the Andes Mountains, near Los Andes city.

Similar to copper, a wide range of arsenic concentration was determined in the soils analyzed; from 2.7 mg As kg⁻¹ in Laguna Verde soil (situated in the center of Chile) to 202 mg As kg⁻¹ in Quillagua soil (situated in Loa valley; in the north of Chile). The average arsenic soil concentration from the north region of Chile, even when the highest values found in Calama and Quillagua were excluded, was higher than in those soils considered as non impacted from the Valparaíso region (27 mg As kg⁻¹ and 3.7 mg As kg⁻¹, respectively) and was as higher as in impacted soils collected in the same region (34 and 19 mg As kg⁻¹ at Puchuncaví and Catemu valley, respectively). It is important to remark that all arsenic concentrations in soils from the north region of Chile exceed the world average concentration reported for this matrix (6 mg As kg⁻¹).³¹ These results are in accordance with those reported by other authors, who have analyzed other environmental matrices from this zone,^{10,33-35} including water soil extracts.⁹ This fact is explained by the presence of arsenic rich volcanic parental rocks, formed during the late Tertiary and the Quaternary, in the Altiplano region,^{4,5,25} and/or by the irrigation of agricultural soils with waters containing high arsenic concentration. High arsenic concentration in water from the north of Chile have been reported.^{10,11,33,35}

The arsenic concentration in soils from the north area in Chile ranged between 9 and 202 mg As kg⁻¹. As can be seen in Fig. 2, Calama (A2) and Quillagua (A3) soils, both from the second region, presented arsenic concentration that greatly exceed the critical concentration in soil (20–50 mg As kg⁻¹).³¹ Quillagua (202 mg As kg⁻¹) presented the highest value, it is up to seven times the average concentration in the area, showing a clear pollution event in this site. This pollution is

attributed to the fact that Calama and Quillagua are sites irrigated with water from the Loa River, that receives the Salado River as an effluent (see Fig. 1), which has a genetic relation with the geothermal field "El Tatio", contaminated naturally with this element. Alonso has reported arsenic concentrations as higher as 40 mg As L⁻¹ in water from El Tatio, 14 mg As L⁻¹ in the origin of Salado River and 0.8 mg As L⁻¹ in Loa River, near to Calama city, after its junction with Salado River.¹⁰ However, the contamination of this river by waste discharges from industrial copper mining processes developed in its vicinity cannot be discarded. It has been demonstrated that high arsenic concentrations are also present in the vegetables cultivated in soils irrigated with this water. Recently, Queirolo *et al.* has determined a very high As content in corn from Socaire (1850 µg kg⁻¹) and in potatoes from Talabre (860 µg.kg⁻¹), two villages located in the Altiplano region, close to active volcanoes.³⁴ On the other hand, the higher arsenic concentration in soils from Quillagua than Calama can be related to the increase of saline concentration in the Loa river water produced by evaporation occurring along the long run on this extreme arid zone.

The highest arsenic concentrations in soil from the Valparaíso region were found in the Puchuncaví valley. Here in all sampled soils, except Nogales (P5), the arsenic concentration were into or exceeded the reported critical toxicity values. Moreover, a clear decrease was observed for arsenic concentration in soils with the distance from "Las Ventanas" industrial complex (Figure 3A, As (mg kg⁻¹) = 75 distance^{-0.49} (km); $R^2 = 0.9145$), with a similar behavior as copper. This fact shows that both elements have the same sources, the copper smelter and the coal-fired thermoelectric plant, located in the Puchuncaví valley. It has been demonstrated that copper smelters and coal-fired thermoelectric plants are the most important anthropogenic sources of arsenic in the environment (40% and 20% of the total anthropogenic input, respectively); the atmospheric deposition through vapor and particulate phase being the principal way for arsenic to reach soils.³¹ On the contrary, the arsenic concentrations in soils from Catemu valley were only slightly higher than the critical concentration, and ranged between 11 and 21 mg As kg⁻¹. In this area the correlation between arsenic concentration in soils and the distance from the copper smelter was not so clear, showing a minor impact produced by this anthropogenic source on the valley. This fact can be explained taken into account that at the Chagres smelter (Catemu valley) several actions were taken sooner than at Las Ventanas, in order to decrease the total emissions from the smelter, especially of airborne particulates.

The arsenic concentrations of soils collected next to Quillota city (Q1 to Q3), were not included in the average value for those considered as non-impacted soils from Valparaíso region (Casablanca, Las Tablas and Laguna Verde). These soils (Q1–Q3) have approximately 21 mg As kg⁻¹, values clearly out of the range found for the non impacted soils (2.7–4.7 mg As kg⁻¹). The use of pesticides and herbicides, which are applied in orchards and soils to control insect pests and to defoliate; or by the use of phosphate fertilizers, both recognized as arsenic sources in agricultural soils,³¹ have increased the arsenic concentrations in these soils. However, these soils are irrigated with waters from Aconcagua River, that could be contaminated by copper mining. A similar pattern was observed for the copper concentrations in these soils.

As for arsenic, the average concentration of antimony in soil collected in the north of Chile (excluding Calama and Quillagua soils), was higher than in non-impacted ones from Valparaíso region (2.4 mg Sb kg⁻¹ and 1.2 mg Sb kg⁻¹, respectively), but for this element the difference was less significant as for arsenic (2 and 7.3 respectively). However, the north average antimony concentration was higher than the reported world average concentration (1 mg Sb kg⁻¹).³¹

Similar to arsenic, high antimony concentrations were determined for soils from Puchuncaví and Catemu valleys (1.8–6.7

and 3.7–4.1 mg Sb kg⁻¹, respectively). These results permit the conclusion that, as well as for copper and arsenic, the copper mining activity and coal-fired thermoelectric plants placed in Puchuncaví and Catemu valleys, have contaminated soils located in their vicinity with antimony.

As can be seen in Fig. 2, a similar pattern to arsenic was obtained for the antimony concentration in soils collected in Calama and Quillagua (11 ± 1 mg Sb kg⁻¹), both soils have the highest values among all sampled soils, and exceed the antimony critical concentration in soil (5–10 mg Sb kg⁻¹).³¹ This probably indicates that the contamination by antimony and arsenic in both sites was related to natural lixiviation of their compounds naturally present in this zone, beside the copper mining activity developed in the area. However, a significant difference was obtained for arsenic/antimony concentration ratios in both soils, 18.4 in Quillagua and 9.6 in Calama (this fact was similar for the arsenic/copper ratios: 5.8 and 2.3, respectively). This behavior clearly shows that Quillagua soil has received the impact of other arsenic sources.

In the Valparaíso region, as for the other elements, the highest antimony concentrations were determined in soils from Puchuncaví valley. In this valley, with the exception of Nogales, the antimony concentrations in all soils were into the critical range. Furthermore, a clear decrease in the antimony concentration with the distance from the industrial complex was observed (Fig. 3B), $Sb \text{ (mg kg}^{-1}\text{)} = -0.2 \text{ distance (km)} + 7.1$, $R^2 = 0.9880$. However, in this case the linear model was most appropriate to represent this behavior. The difference with the copper and arsenic pattern is probably due to the presence of antimony compounds in the smallest airborne particles (less heavy), permitting antimony to travel long distances. Zheng *et al.*, have stated that antimony is associated with airborne particulate matter at a concentration twice as high as arsenic in this material, collected in Tokio.³⁶ This results demonstrate that antimony, as well as arsenic and copper, has reached these soils by atmospheric deposition of particulate material produced by the industrial activities.

Although the concentrations of antimony in soils collected in the Catemu valley were higher than in non-impacted soil (*i.e.* Casablanca, Las Tablas and Laguna Verde), these values never exceed the critical range. Moreover, in this valley none of the elements in this study showed a clear pattern relating to the distance to the smelter, and only 8% of relative standard deviation was obtained in the antimony concentrations for soils from this valley. These results shows that, in contrast to the industrial complex placed at Puchuncaví valley, the copper smelter in the Catemu valley has produced a minor impact on soils.

In soils collected near to Quillota city, as for arsenic, the antimony concentrations were higher than in non-impacted soils from Valparaíso region (1.8–2.1 mg Sb kg⁻¹). Since the natural association between antimony and arsenic, the sources described previously for the high arsenic concentration in these soil, are also extensive to antimony.

Cu-As, Cu-Sb and Sb-As relationships in soils

Fig. 4 presents the relationships between the concentrations of copper and arsenic, copper and antimony and antimony and arsenic in the analyzed agricultural soils. As can be seen in Fig. 4A, 4C and 4E, the values for Calama and Quillagua soils (black triangles and circles, respectively) were clearly outliers of the trend followed by the other samples. This fact clearly show that these soils were polluted by irrigation with naturally contaminated water from the El Tatio geothermal field and by mining activities developed in this zone. In order to eliminate the influence of these extreme values on the correlation coefficients values, the evaluations were carried out without these outlier values. Statistically significant correlations have been found in all cases, especially in Cu-Sb relationships, corroborating the natural association between these elements in the environment.

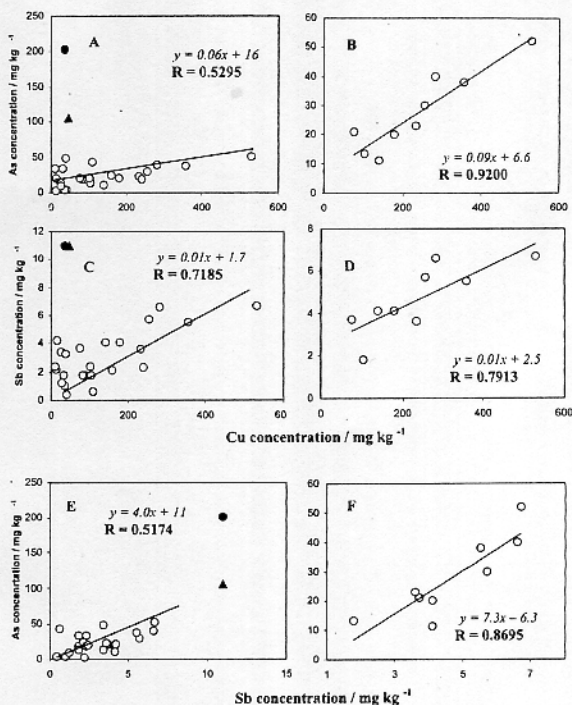


Fig. 4 Relationships between the concentrations of copper and arsenic, copper and antimony and antimony and arsenic in agricultural soil. A, C and E plots include all soils. B, D and F plots include only soils collected in the impacted Puchuncaví and Catemu valleys (● Quillagua soil, ▲ Calama soil).

It is important to remark that better Cu-As, Cu-Sb and Sb-As correlations were found when only soils from Puchuncaví and Catemu valleys were considered (see values in Fig. 4B, 4D and 4F). Summarizing, the significant correlation values determined, permits the corroboration of the association between the high concentration of arsenic and antimony determined in these soils, and the copper smelter activity carried out in the valleys.

Conclusions

Wide concentration ranges were found for copper, arsenic and antimony in the 26 soils sampled from three different regions in Chile. The copper concentrations in non-polluted soils from the north and central zone of Chile were similar. Three sites from the north region (Mamiña, Chiu-Chiu and Antofagasta Norte) have copper concentrations as high as 100 mg kg⁻¹, demonstrating the contamination degree by this element. These copper concentrations exceed the critical concentration in soils. High arsenic concentrations were found in all soils from the north region, specially at Calama and Quillagua sites, both located in the Loa valley. This contamination is produced by the irrigation waters, coming from the Salado River, with its origin in the geothermal zone El Tatio, located in the Chilean Altiplano. These sites have also the highest antimony concentrations. The data showed that soils from Puchuncaví and Catemu valleys have an important contamination degree by copper, arsenic and antimony. In the first area, the concentration of these elements exceeded the reported critical values for this matrix; instead at Catemu valley, only the copper concentration was higher than this value. Moreover, at Puchuncaví valley a clear decrease was observed for the three elements concentrations in soils, on the function of the distance from the industrial complex Las Ventanas. These results reflect the impact produced by copper mining activities developed in both valleys. Statistically significant correlation was found for

Cu-Sb in all soils; more significant Cu-As, Cu-Sb and Sb-As correlations were evaluated for soils from Puchuncaví and Catemu valleys. Based on the results, it can be definitely confirmed that high copper, arsenic and antimony concentrations in these soils coming from the same pollution sources, the copper industry and the thermoelectric power plant. Finally, these results give reliable information about the concentrations of three important environmental pollutants commonly associated with mining industries, activity of great importance in Chile.

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