

Spatial distribution of copper, organic matter and pH in agricultural soils affected by mining activities

R. Aguilar¹, C. Hormazábal¹, H. Gaete², A. Neaman^{1,3,*}

¹Laboratorio de Suelos y Análisis Foliar, Facultad de Agronomía, Pontificia Universidad Católica de Valparaíso, Casilla 4-D, Quillota, Chile. ²Departamento de Biología y Ciencias Ambientales, Facultad de Ciencias, Universidad de Valparaíso, Gran Bretaña 1111, Playa Ancha, Valparaíso, Chile. ³Centro Regional de Estudios en Alimentos Saludables (CREAS), Región de Valparaíso. * Corresponding author: E-mail: alexander.neaman@ucv.cl, Phone: 56-32-2274537, Fax: 56-32-2274570

Abstract

The Aconcagua River Basin, located in north-central Chile, is an important agricultural region of the country. However, several copper mining industries are also located in this basin. A total of 103 topsoil samples were collected at varying distances from mining industries. There were no statistically significant differences between the sampling areas with regard to organic matter content and copper concentration. However, the sampling areas were significantly different with regard to soil pH. Soils of the Putaendo sampling area exhibited the lowest pH values (mean of 6.3), while the highest pH values (mean of 7.1) were measured in the Catemu – Chagres sampling area. In the sampling areas where mining activities were absent, the total copper concentrations ranged from 70-155 mg kg⁻¹. These concentrations are a result of the geological setting and/or of applications of copper-containing fungicides. High copper concentrations (above 700 mg kg⁻¹, with a maximum of 4000 mg kg⁻¹) were generally observed near mining activities or in areas where mining activities were located nearby and upstream. In these sampling areas, the copper concentrations differed by an order of magnitude in nearby locations. These high and heterogeneously-distributed copper concentrations most likely resulted from either modern or former mining activities.

Keywords: trace elements, metals, agriculture, mining, smelting.

1. Introduction

The Aconcagua River Basin (ARB) is located in north-central Chile in the Valparaíso Region, between 32°30' and 33°07' latitude south (Figure 1), with an area of ~7600 km². The ARB is one of the most important agricultural regions of Chile (ODEPA-CIREN, 2002; IGM, 2003). However, Chile is the foremost copper producer in the world (Comisión Chilena del Cobre, www.cochilco.cl), and several important copper mining industries are located in the

ARB. The most important of these industries are the El Soldado (near Nogales) and Andina complexes (near Saladillo, in the high Andes, ~3500 m above sea level). These complexes include mines and ore concentration/leaching plants. In addition, there are several smaller mines, concentration/leaching plants, and mine dumps distributed throughout the basin, and a copper smelter at Chagres (near the town of Catemu) (Arancibia, 2002; Lara and Romo, 2002).

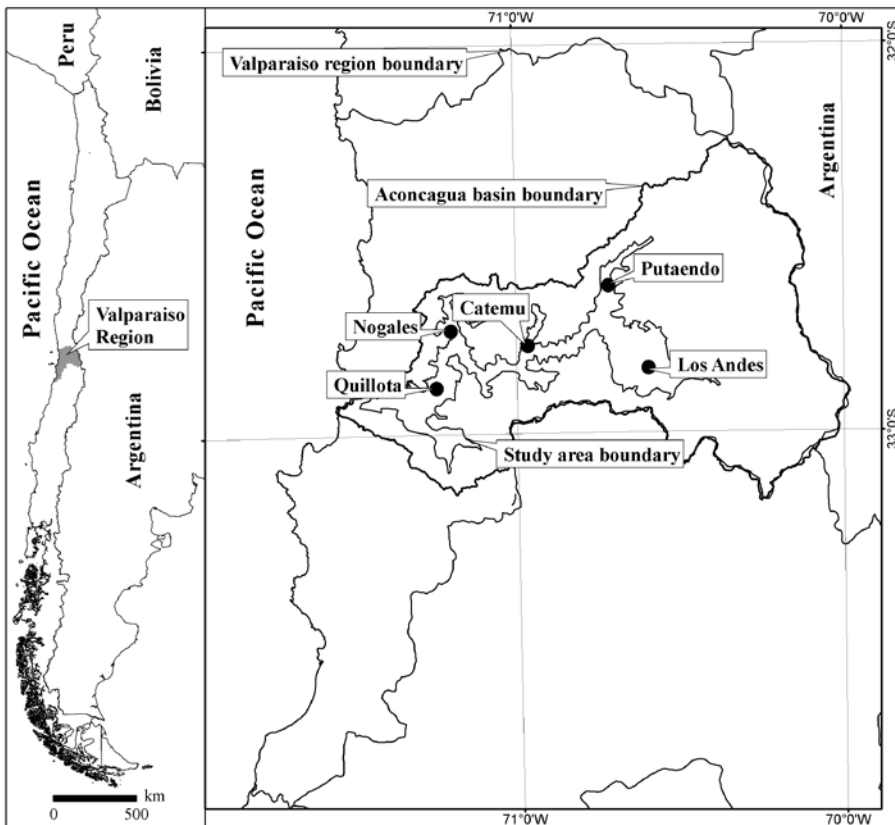


Figure 1. Location of the Aconcagua River Basin. The study was limited to arable soils located on landforms with slopes of less than 15%.

The environmental problems historically associated with copper mining are widely known, particularly in relation to the contamination of agricultural soils by metals (González *et al.*, 1984; Ginocchio, 2000; De Gregori *et al.*, 2003). Copper is the main contaminant in the soils of copper mining areas in Chile (Goecke *et al.*, 2011). Copper is an essential micronutrient to all organisms but is toxic at certain concentrations (McBride, 1994; Adriano, 2001).

Environmental (or ecological) risk is defined as “the potential for adverse effects on living organisms associated with pollution of the environment by effluents, emissions, wastes, or accidental chemical releases; energy use; or the depletion of natural resources” (U.S. Environmental Protection Agency, Terms of Environment: Glossary, Abbreviations and Acronyms, www.epa.gov/OCEPATERMS). It is well known that the total concentration of a metal in a soil is not sufficient to predict the potential ecological risk that it represents (McBride, 1994; Sauvé *et al.*, 1998; ISO 17402, 2008). Ecological risk is more related to the bioavailability of the metal that, in turn, is related to the chemical form in which it is found in the soil (Adriano, 2001). The National Research Council (2003) defines bioavailability as the fraction of the total element that is available to the receptor organism.

Although the total metal concentration in the soil is not a good indicator of the elements bioavailability, total concentrations are still used by legislations in many countries (Ewers, 1991). In some cases, legislations consider soil properties that affect metal bioavailability. For instance, the Council of the European Communities (2009) and the UK (1989) consider the soil pH for maximum concentrations of metals in soils on which sewage sludge is applied.

Chile currently does not have any legislation on the maximum permissible concentrations of metals in soils. Any future legislation should distinguish between soils where metals are present but do not represent a

risk from those that, at similar total concentrations of metals, do represent significant ecological risks (Ávila *et al.*, 2009). In other words, future legislation should consider soil properties that affect metal bioavailability, such as soil pH and organic matter content (Adriano, 2001; Sauvé, 2003; Kabata-Pendias, 2004).

To establish the maximum permissible concentrations of copper in soils, its bioavailability can be assessed by exposing organisms, e.g., plants, microorganisms, and invertebrates, to soil to monitor the effects of bioavailable copper (ISO 17402, 2008). In such types of experiments, care should be taken so that soils have wide ranges of copper concentration, pH, and organic matter content. However, little data are available on the spatial distribution of these soil characteristics in agricultural soils of the ARB. Therefore, the main objective of the present study was to determine the spatial distribution of copper, pH, and organic matter in the agricultural soils of the ARB. Additionally, for metal bioavailability tests with organisms, it is important to sample soils with different sources of contamination because different types of mine wastes have different solubilities (Ginocchio *et al.*, 2006). Therefore, the second objective of the present study was to estimate the possible sources of contamination. The information generated from this study will form the basis for choosing locations for soil sampling in future studies aimed at assessing copper bioavailability.

2. Materials and methods

Using a Geographical Information System (GIS) and available GIS databases, the agricultural soils of the ARB were clustered into 8 sampling areas (Table 1). The study was limited to arable soils located on landforms with slopes less than 15% (Figure 1). These boundaries included the agricultural soils that have traditionally been irrigated by gravity.

Table 1. Sampling locations and chemical properties of the studied soils. Different letters in the pH column indicate significant differences between the sampling areas (Tukey test, $p < 0.001$). There were no differences (ANOVA, $p > 0.05$) between the sampling areas with regard to organic matter (OM) content and total copper concentration.

Sample	Coordinates		WGS 1984 UTM H19S		Crop	pH	OM, %	Total copper, mg kg ⁻¹
	W	S	E	N				
Quillota sampling area								
106	70°29'15"	32°51'19"	294404	6363683	Fallow	7	5.4	96
107	70°30'32"	32°50'53"	287993	6356616	Cabbage	6.9	5.9	100
108	70°32'25"	32°49'59"	289484	6355597	Fallow	7.3	5.1	91
109	70°33'50"	32°44'1.5"	291200	6358418	Fallow	7.1	5.6	98
110	70°33'44"	32°44'5"	291987	6359551	Fallow	6.8	5.7	154
Median						7.0	5.6	98
Mean						7.0 ab	5.5	108
STD						0.2	0.3	26
CV, %						3	6	24
Nogales sampling area								
68	71°11'40"	32°38'59"	294161	6385402	Avocado	6.8	2.4	115
70	71°11'47"	32°39'3"	293979	6385277	Bean	7	3.2	111
72	71°11'56"	32°38'51"	293771	6385618	Bean	6.9	4.8	253
73	71°11'14"	32°38'39"	294841	6386016	Bean	6.8	4.4	401
74	71°11'56"	32°38'35"	293732	6386139	Lemon	7.9	0.8	4087
76	71°12'12"	32°39'41"	293355	6384094	Walnut	6.8	3.9	670
82	71°7'5"	32°42'58"	301480	6378195	Lemon	7.1	4.7	122
83	71°6'38"	32°42'44"	302192	6378638	Alfalfa	6.5	4.3	128
84	71°6'43"	32°42'33"	302038	6378951	Fallow	6.9	6.1	130
85	71°6'36"	32°42'32"	302232	6379007	Beans	6.3	3.2	90
120	70°33'48"	32°44'5"	297663	6370833	Avocado	7.2	4.7	151
121	70°37'46"	32°44'55"	294947	6376708	Cabbage	6.8	4.5	116
122	71°11'17"	32°43'41"	294949	6376705	Tomato	6.1	6.6	159
123	71°10'16"	32°44'23"	296563	6375439	Fallow	6.8	4.1	270
124	71°9'49"	32°44'59"	297301	6374337	Fallow	6.6	4.2	192
Median						6.8	4.3	151
Mean						6.8 ab	4.1	466
STD						0.4	1.4	1013
CV, %						6	34	217

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Sample	Coordinates		WGS 1984 UTM H19S		Crop	pH	OM, %	Total copper, mg kg ⁻¹
	W	S	E	N				
Catemu – Llay-Llay sampling area								
53	70°54'30"	32°51'42"	321434	6362426	Fallow	6.9	3.4	114
54	70°53'34"	32°51'41"	322898	6362461	Peach	6.9	2.8	131
55	70°53'35"	32°51'52"	322861	6362136	Lemon	6.7	0.6	746
56	70°53'18"	32°51'34"	323304	6362691	Fallow	6.8	3	99
57	70°55'33"	32°50'32"	319751	6364553	Pears	6.7	2.9	125
58	70°55'41"	32°50'17"	319551	6365006	Alfalfa	7.3	2.9	119
59	70°55'11"	32°50'40"	320329	6364311	Fallow	7	3	105
60	70°54'53"	32°50'23"	320777	6364829	Corn	7	3.1	247
61	70°55'01"	32°50'26"	320608	6364758	Onion	7.1	3.2	183
62	70°54'52"	32°50'49"	320841	6364052	Grape	6.9	3.4	230
102	70°25'32"	32°51'30"	317650	6363745	Fallow	7.4	3	80
104	70°25'59"	32°51'21"	320523	6362226	Fallow	6.7	6.6	147
105	70°26'29"	32°51'12"	315679	6364444	Fallow	7.2	3.4	140
Median						6.9	3.0	131
Mean						7.0 ab	3.2	190
STD						0.2	1.3	174
CV, %						3	40	92
Catemu – Panquehue sampling area								
99	70°49'11"	32°45'32"	329546	6373941	Fallow	7.1	3.2	167
100	70°25'01"	32°51'33"	327253	6372373	Oat	6.8	3.6	115
101	70°24'55"	32°51'30"	325600	6370868	Onion	7.4	3.8	108
Median						7.1	3.6	115
Mean						7.1 ab	3.5	130
STD						0.3	0.3	32
CV, %						4	9	25
Catemu – Ñilhue sampling area								
17	70°58'24"	32°46'28"	315164	6371966	Grape	7.1	2.4	180
18	70°59'43"	32°46'5"	313918	6372656	Grape	6.8	4.5	629
19	70°59'13"	32°46'13"	313903	6372422	Fallow	6.6	5.6	1003
20	70°57'52"	32°45'15"	315938	6374218	Grape	6.3	1.6	445
21	70°58'03"	32°43'51"	315643	6376827	Alfalfa	6.6	3.4	470
22	70°57'42"	32°44'00"	316170	6376573	Grape	6.4	3.4	257
23	70°57'32"	32°44'34"	316462	6375492	Wheat	6.2	2.7	249

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Sample	Coordinates		WGS 1984 UTM H19S		Crop	pH	OM, %	Total copper, mg kg ⁻¹
	W	S	E	N				
24	70°56'49"	32°44'12"	317563	6376199	Tobacco	6.7	1.9	231
25	70°56'33"	32°43'17"	317958	6377906	Orange	6.3	2.4	278
26	70°56'18"	32°42'48"	318334	6378786	Fallow	6.5	2.3	275
27	70°54'43"	32°41'42"	320798	6380861	Olive	6.9	4.3	2411
28	70°55'56"	32°41'0.5"	318857	6382158	Almond	6.6	3.7	457
29	70°56'26"	32°41'12"	318073	6381757	Peach	7	5.4	585
Median						6.6	3.4	445
Mean						6.6 bc	3.4	575
STD						0.3	1.3	596
CV, %						4	39	104
Catemu – Chagres sampling area								
15	70°57'25"	32°47'32"	316737	6370031	Grape	7.6	0.9	155
16	70°58'25"	32°47'11"	315177	6370653	Grape	7.4	9.8	99
30	70°57'3"	32°48'22"	317299	6368509	Alfalfa	6.5	5.6	462
31	70°57'1"	32°48'30"	317408	6368278	Fallow	7.4	4.9	351
32	70°55'46"	32°48'14"	319339	6368769	Fallow	7.2	3.9	119
33	70°55'38"	32°48'23"	319550	6368512	Grape	7.7	4.3	87
34	70°56'58"	32°48'7"	317465	6368953	Avocado	7.1	5.1	918
35	70°57'18"	32°47'28"	316917	6370138	Maize	7	3.1	319
36	70°56'40"	32°47'49"	317920	6369551	Fallow	7.5	2.3	675
37	70°56'23"	32°47'49"	318372	6369531	Alfalfa	6.9	2.2	362
38	70°56'11"	32°47'42"	318661	6369763	Alfalfa	7.1	4	483
39	70°56'7"	32°47'1"	318763	6371019	Fallow	6.7	2.2	492
40	70°54'53"	32°46'42"	320691	6371643	Lettuce	7.1	1.1	208
41	70°53'5"	32°46'46"	323486	6371554	Grape	6.8	14	259
42	70°52'49"	32°46'36"	323915	6371873	Alfalfa	6.7	2.4	387
43	70°53'27"	32°46'26"	322894	6372147	Bean	6.7	2.5	181
44	70°53'48"	32°46'4"	322353	6372839	Bean	6.9	0.9	336
45	70°55'38"	32°47'24"	319520	6370340	Artichoke	7.3	1.4	199
46	70°55'19"	32°46'57"	320008	6371154	Tomato	7.5	1.6	247
47	70°55'39"	32°46'27"	319437	6372073	Bean	6.8	1	535
48	70°57'7"	32°46'36"	317175	6371754	Alfalfa	7.1	4.1	133
49	70°57'58"	32°48'29"	315928	6368249	Tobacco	7.1	5.1	829

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Sample	Coordinates		WGS 1984 UTM H19S		Crop	pH	OM, %	Total copper, mg kg ⁻¹
	W	S	E	N				
50	70°58'5''	32°48'27''	315730	6368311	Fallow	7.1	3.1	599
51	70°59'9''	32°48'34''	314068	6368074	Pasture	7.3	6.3	184
52	70°58'8''	32°48'17''	315638	6368639	Chili	7.3	3	375
Median						7.1	3.1	336
Mean						7.1 a	3.8	360
STD						0.3	3.0	223
CV, %						4	78	62
Putando sampling area								
1	70°43'10''	32°39'38''	338763	6384993	Tobacco	6.1	4.7	90
2	70°42'51''	32°38'0.7''	339215	6388010	Tobacco	6.1	2.2	79
3	70°41'7''	32°36'47''	341880	6390318	Pumpkin	7	4.2	112
4	70°41'46''	32°37'21''	340898	6389258	Almond	6.8	4.3	120
5	70°40'23''	32°34'40''	342957	6394267	Olive	6.1	7.6	87
6	70°40'23''	32°34'40''	342956	6394270	Clover	6.3	5.9	88
7	70°35'12''	32°30'5''	350959	6402876	Walnut	6.8	3.3	73
8	70°38'10''	32°31'30''	346390	6400169	Peach	6.2	3.6	88
9	70°44'11''	32°35'37''	337008	6392400	Peach	6.1	3.8	86
10	70°44'19''	32°36'16''	336846	6391195	Peach	6.3	3.6	115
11	70°44'9''	32°36'35''	337132	6390599	Fallow	6.2	3.1	91
12	70°44'45''	32°39'44''	336301	6384752	Fallow	5.8	2.3	112
13	70°45'23''	32°41'3''	335339	6382340	Fallow	6.5	2.2	84
14	70°46'22''	32°41'38''	333831	6381211	Fallow	6.2	3.4	101
Median						6.2	3.6	89
Mean						6.3 c	3.9	95
STD						0.3	1.5	15
CV, %						5	38	15
Los Andes sampling area								
86	70°25'1.5''	32°51'33''	367419	6363437	Pumpkin	6.1	4.3	140
87	70°24'55''	32°51'30''	367590	6363504	Bean	7	3.2	85
88	70°25'32''	32°51'30''	366617	6363493	Onion	6.3	5.9	641
89	70°25'59''	32°51'21''	365894	6363768	Alfalfa	6.9	4.4	3378
90	70°26'29''	32°51'12''	365127	6364022	Alfalfa	6.6	5.4	971
91	70°29'15''	32°51'19''	360802	6363734	Peach	7.1	5.4	140

Continued...

Sample	Coordinates		WGS 1984 UTM H19S		Crop	pH	OM, %	Total copper, mg kg ⁻¹
	W	S	E	N				
92	70°30'32"	32°50'53"	358819	6364540	Corn	6.7	2.7	304
93	70°32'25"	32°49'59"	355856	6366135	Alfalfa	6.3	3.2	337
125	70°37'47"	32°49'49"	347465	6366320	Watermelon	7.3	2.7	453
126	70°40'44"	32°48'55"	342836	6367921	Bean	6.7	2.5	314
128	70°36'38"	32°49'10"	349264	6367525	Grape	7.4	2.5	167
94	70°33'50"	32°44'1.5"	353448	6377151	Fallow	7	3	725
95	70°33'44"	32°44'5"	353627	6377013	Grape	6.5	4.1	892
96	70°33'48"	32°44'5"	353520	6377016	Grape	6.6	4	755
97	70°37'46"	32°44'55"	347334	6375393	Plum	6.5	3.3	670
Median						6.7	3.3	453
Mean						6.7 b	3.8	665
STD						0.4	1.1	804
CV, %						6	30	121

In each sampling area, locations of mining industries were considered possible sources of soil contamination by copper. A total of 103 topsoil samples (0-20 cm) were collected at varying distances from these industries. The samples were processed by drying them at 60°C, grinding aggregates in a granite mortar, and sieving them to obtain a fraction of <2 mm.

Total copper concentrations in the soils were determined by atomic absorption spectroscopy following digestion of the samples with nitric-perchloric-hydrofluoric acid mixtures (Maxwell, 1968; Jeffery, 1970). The accuracy of the analyses was assessed by including certified reference soils. The deviations in the measured and certified values were less than 10%. A solution of 0.1 M KNO₃ was used as an extractant at a soil:solution ratio of 1:2.5 g/ml for the determination of soil pH. The organic matter content was determined by wet combustion with sodium dichromate and sulphuric acid without heat application (Sadzawka *et al.*, 2006). All analyses were performed in duplicate, and average val-

ues are reported in Table 1. The deviations in the values obtained from the duplicate runs were less than 10%.

Median, mean, standard deviation (STD), and coefficient of variation (CV, % = STD · 100% / mean) were calculated for the pH, organic matter content, and total copper concentration for each sampling area (Table 1). Variance analysis (ANOVA) was used to compare the sampling areas with regard to these soil characteristics. Statistically significant differences were determined using a Tukey test. All of the analyses were performed using the programs Excel 2003 and Minitab 15.

3. Results and discussion

3.1. Spatial distribution of organic matter and pH in the ARB soils

There were no differences (ANOVA, $p > 0.05$) between the sampling areas with regard to organic matter content. The mean values for all areas were in the range of 3.2-5.5%. The spatial distribution of organic

matter in each area was heterogeneous, exhibiting coefficients of variation of as high as 78% (Table 1).

The sampling areas were significantly different with regards to pH (Tukey test, $p < 0.001$). Soils of the Putaendo sampling area exhibited the lowest pH values (mean of 6.3), while the highest pH values (mean of 7.1) were from the Catemu – Chagres sampling area. The spatial distribution of pH in each area was homogeneous, exhibiting coefficients of variation up to 6% (Table 1).

3.2. Background total copper concentrations in the ARB soils

Although the total metal concentration in the soil is not a good indicator of the elements bioavailability, total concentrations are still used by legislations in many countries (Ewers, 1991). For instance, the Canadian Council of Ministers of the Environment (2007) established a total copper concentration of 63 mg kg⁻¹ as a soil quality guideline for agricultural land use.

The total copper concentrations were in the range of 90-155 mg kg⁻¹ in the Quillota sampling area, where the only mining activity is a small-scale mine (Figure 2, Table 2). The spatial distribution of copper was relatively homogeneous, exhibiting a coefficient of variation of 24% (Table 1). In agreement with these findings, De Gregori *et al.* (2003) reported that the total copper concentrations in three agricultural soils near Quillota were in the range of 80-160 mg kg⁻¹. Similar concentrations in the range of 70-140 mg kg⁻¹ were observed along the El Carretón Creek, where the only mining activity is a small-scale mine (Figure 3); at sampling point 7 along the Putaendo River, which is upstream of copper mining activities (Figure 5); and along the Colorado River, where mining activities are absent (Figures 6 and 7). Based on the virtual absence of mining activities in these locations, total copper concentrations in the range of 70-155 mg kg⁻¹ could be considered to be the background concentrations for the alluvial soil of the ARB.

Table 2. Copper mining activities in the Aconcagua River Basin (Arancibia, 2002; Lara and Romo, 2002).

Sampling area	Large-scale mines/plants	Small-scale mines/plants	Mining dumps	Smelter slag
Quillota	-	1	-	-
Nogales	3	3	5	-
Catemu – Llay-lLAY	-	2	1	-
Catemu – Panquehue	-	1	-	-
Catemu – Ñilhue	-	18	3	2*
Catemu – Chagres	-	-	-	1**
Putaendo	-	13	1	-
Los Andes	-	3	-	-
Blanco River (to the southeast of Los Andes)	4	1	3	-

* Former smelters

** Active smelter

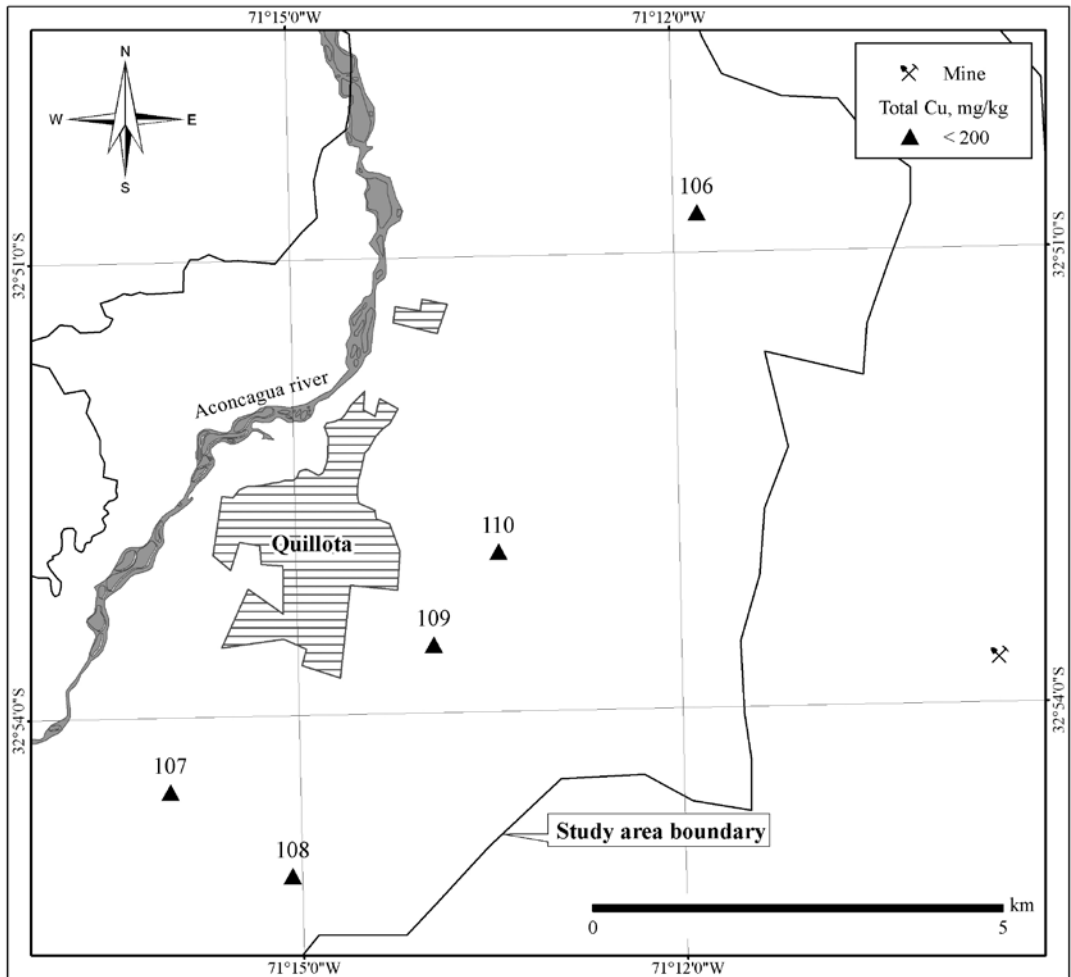


Figure 2. Spatial distribution of total soil copper concentrations in the Quillota sampling area.

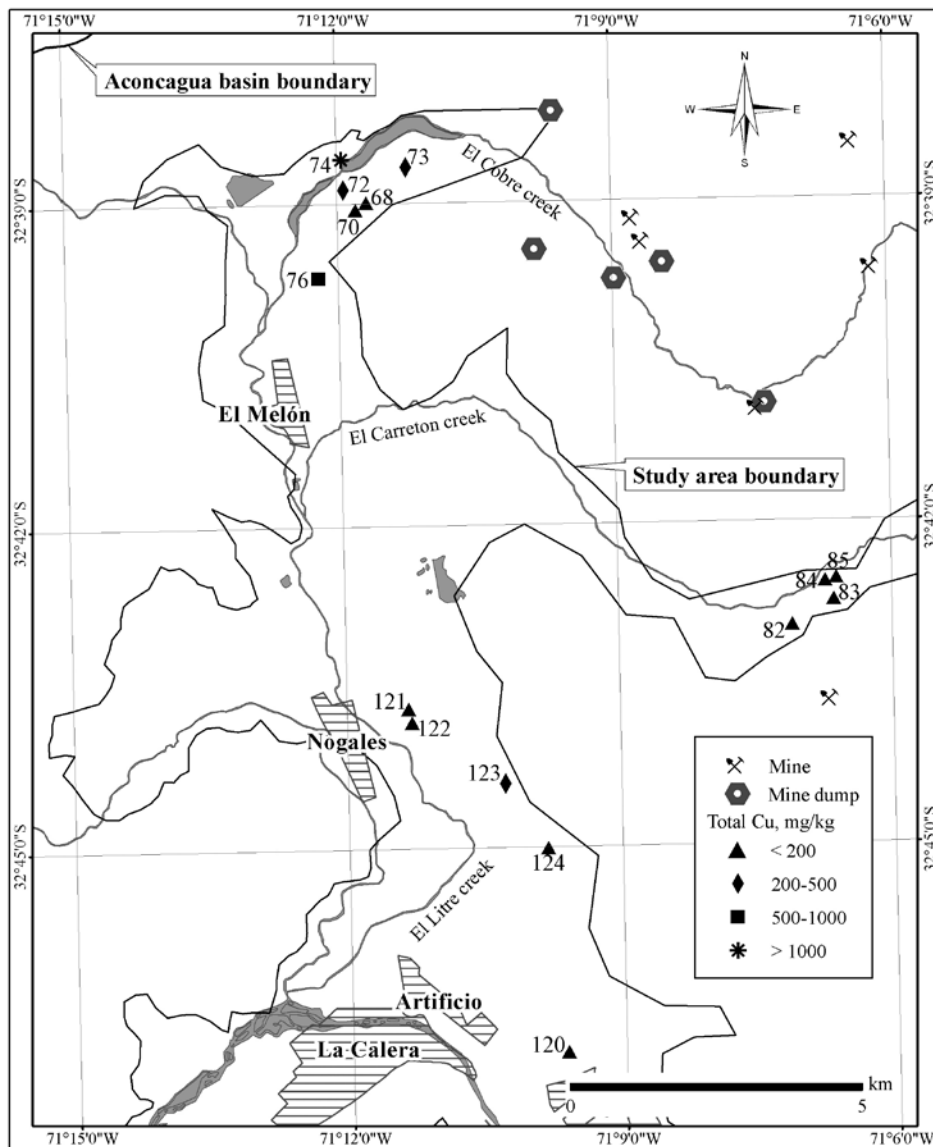


Figure 3. Spatial distribution of total soil copper concentrations in the Nogales sampling area.

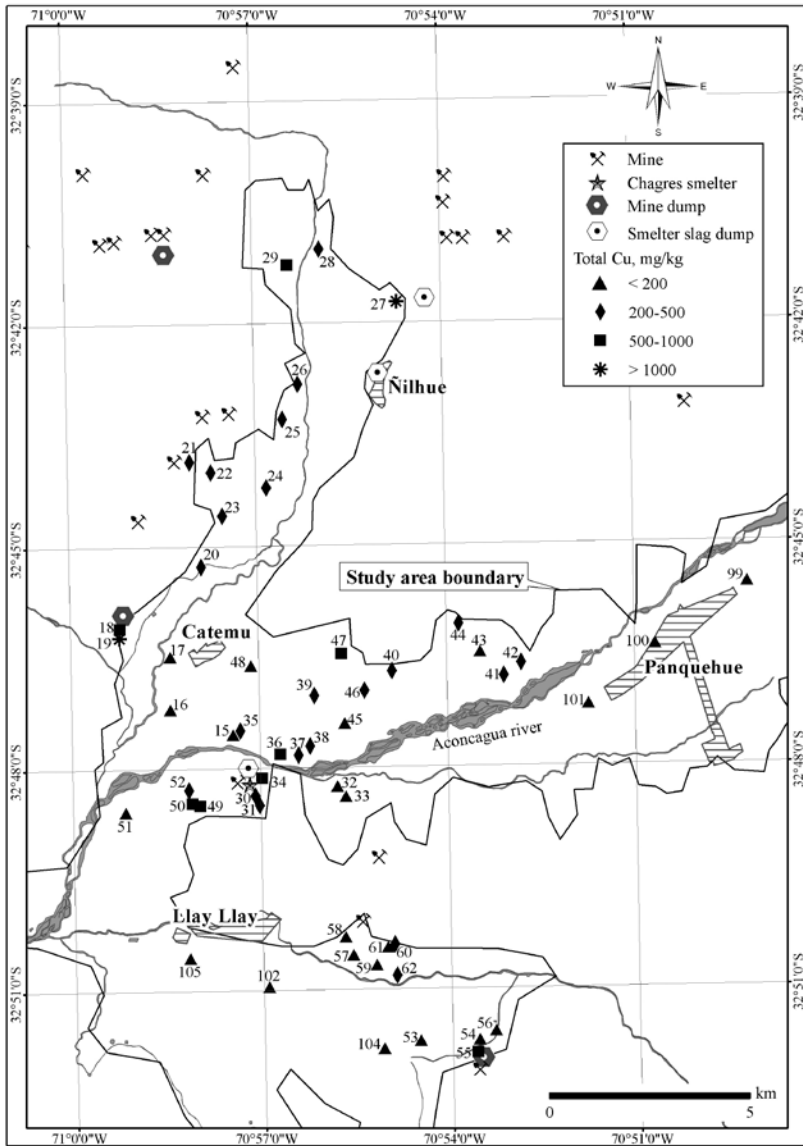


Figure 4. Spatial distribution of total soil copper concentrations in the Catemu – Llay-Llay, Catemu – Panquehue, Catemu – Ñilhue, and Catemu – Chagres sampling areas.

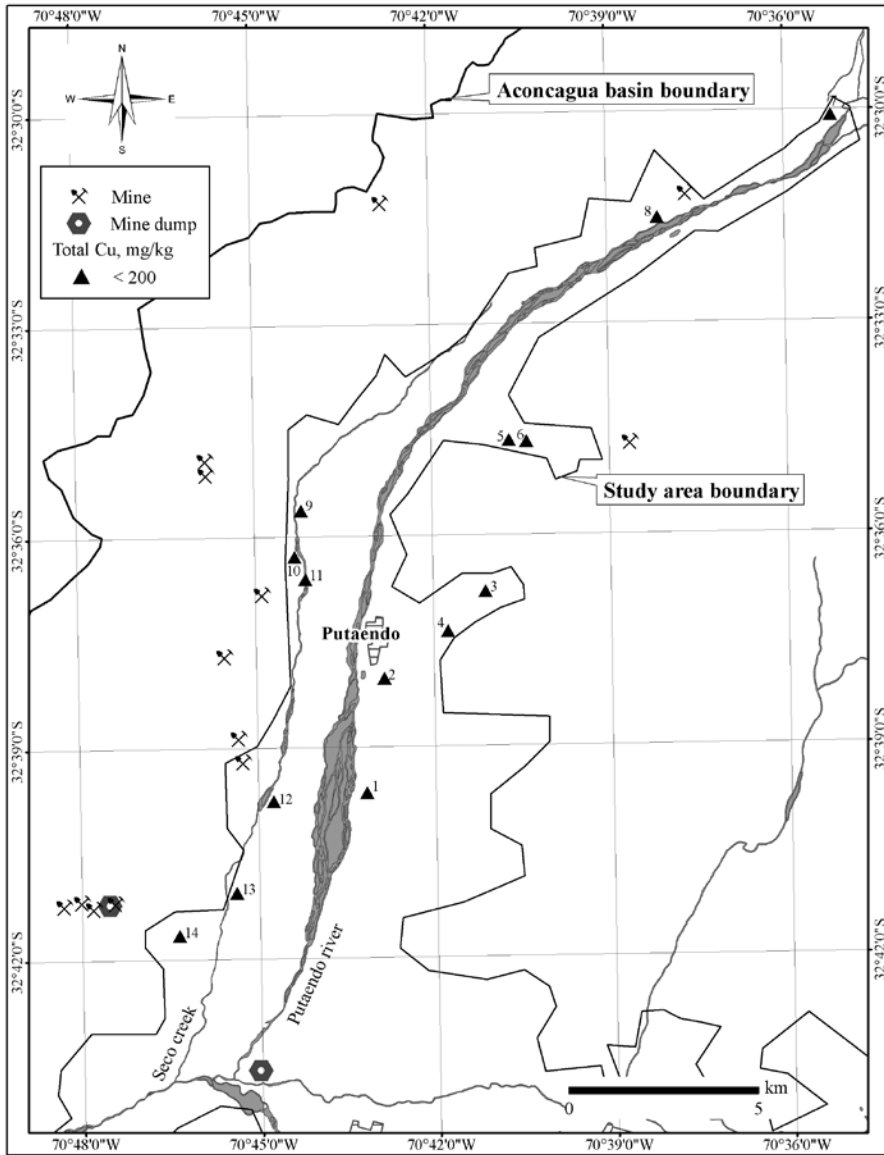


Figure 5. Spatial distribution of total soil copper concentrations in the Putaendo sampling area.

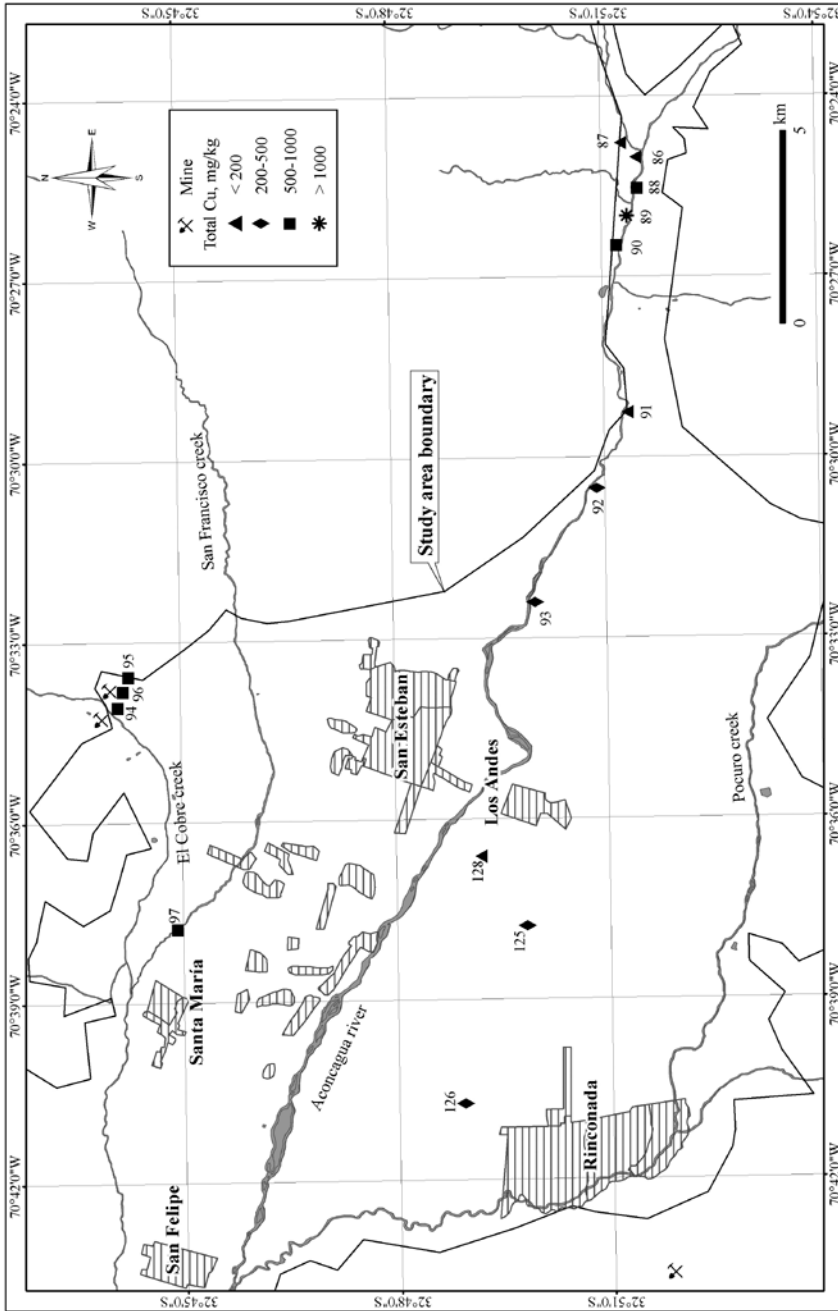


Figure 6. Spatial distribution of total soil copper concentrations in the Los Andes sampling area.

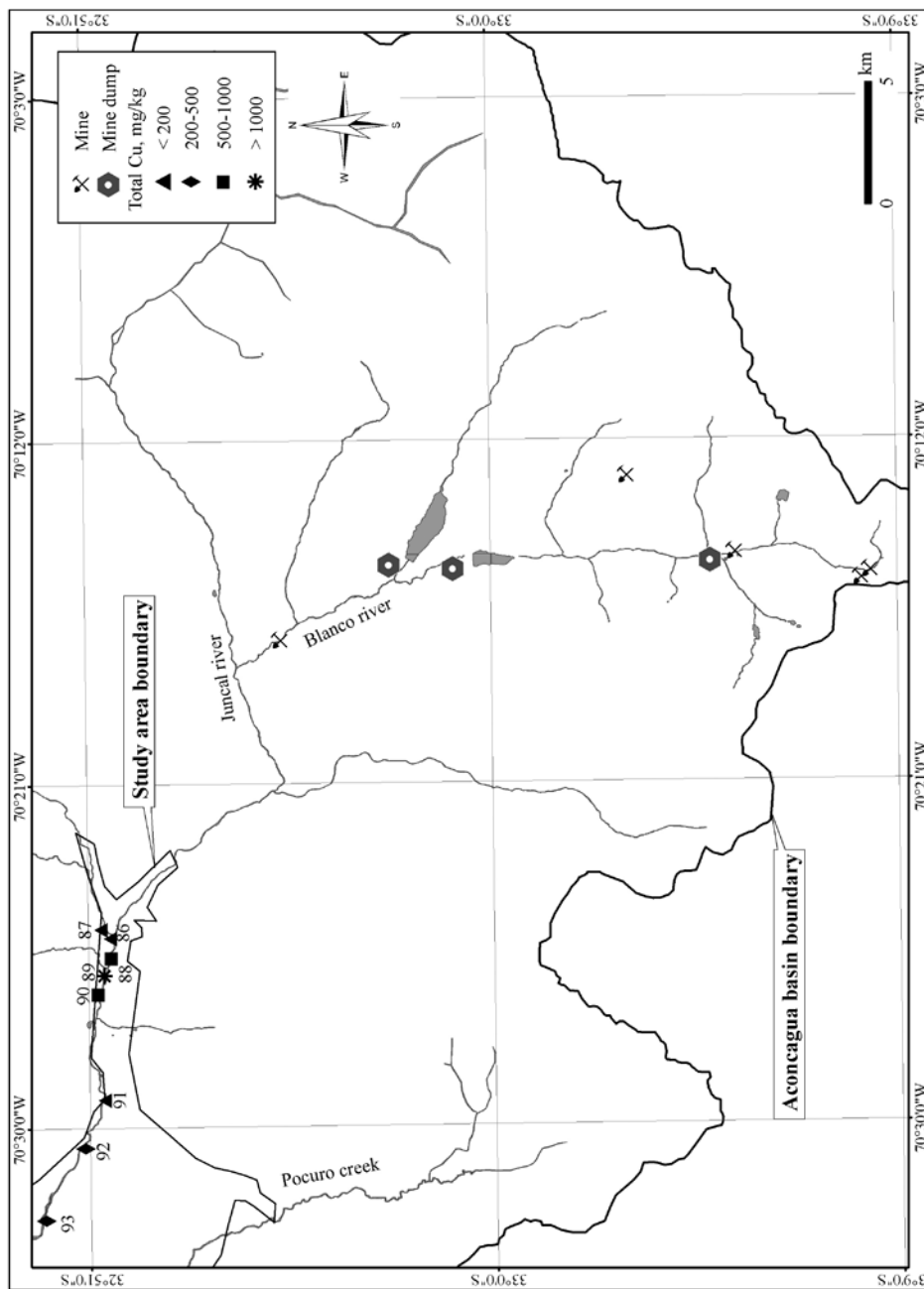


Figure 7. Locations of mines and mine dumps of the Andina mining complex outside of the study area.

Nonetheless, the natural copper concentrations in the soils of the ARB are expected to be greater than the average soil copper concentrations from the rest of the world due to its geological setting. In agreement with this claim, we note that the total copper concentration of world soils averages 30 mg kg^{-1} (Adriano, 2001). Thus, international legislations for the assessment of the degree of soil contamination should not be applied to Chile because of its natural abundance in the soils.

It could also be argued that the relatively high total soil copper concentrations in the above-mentioned locations are a result of applications of copper-containing fungicides. For example, Pietrzak and McPhail (2004) reported that the use of copper-based fungicides in Victoria (Australia) has increased the total copper concentration in some vineyard soils to 250 mg kg^{-1} compared to background concentrations of approximately 10 mg kg^{-1} .

To estimate the effect of fungicides on soil copper concentrations, we assumed the following hypothetical conditions: a recommended rate equivalent of up to 3 kg copper per fungicide application (AFIPA, 2002 - 2003), 4 applications per year over 40 years, a soil depth of 20 cm , a soil bulk density of 1200 kg m^{-3} , and the absence of the leaching of copper from the soil. Based on data from preliminary experiments, approximately 50% of the copper sprayed on crops accumulates in the soil, while the rest is retained by the crops themselves (Sergio González, INIA La Platina, personal communication). Under these conditions, fungicides would contribute to soil copper concentrations of up to 100 mg kg^{-1} . However, more experiments are necessary to determine the percentage of fungicide retention by the crops.

Nonetheless, the contribution of copper-containing fungicides to the soil copper concentrations

is expected to be similar at all sampling locations because the application of fungicides is not attributed to a specific crop or crop type; rather, it is a very common practise for several vegetable and fruit crops in Chile (AFIPA, 2002 - 2003). For this reason, we propose that, independent of the sources of soil copper from the above-mentioned locations, the total copper concentrations in the range of $70\text{-}155 \text{ mg kg}^{-1}$ should be considered to be the background soil concentration.

3.3. Spatial distribution of copper in the ARB soils

The spatial distribution of copper concentrations in the soils of the ARB could predominantly be influenced either by mining activities or the geological processes of erosion and transport of copper-rich rocks. For example, Schalscha and Ahumada (1998) and Gaete *et al.* (2007) reported that copper in the Aconcagua River waters was present not only in a soluble form but also as a suspended solid phase.

If the copper concentrations in the alluvial soils of the ARB were controlled by geological processes, we would expect to observe a homogeneous distribution of the soil copper concentrations in nearby locations. In contrast, a heterogeneous distribution of copper concentrations would be indicative of anthropogenic impacts.

In the following discussion, the effects of copper mining activities (Table 2) and the erosion of copper-rich rocks on copper distribution throughout the soils will be evaluated separately for each sampling area. There were no differences (ANOVA, $p > 0.05$) between the sampling areas with regard to the total copper concentration. To simplify the following discussion, the concentration/leaching plants will be referred to as “mines”.

Nogales sampling area

In the Nogales sampling area (Figure 3), the spatial distribution of copper was very heterogeneous, exhibiting a coefficient of variation of 217% (Table 1), which is indicative of anthropogenic impacts. The highest (up to 4000 mg kg⁻¹) total copper concentrations were observed in the northern section along the El Cobre Creek. Most likely, these high copper concentrations resulted from the destruction of the mining reservoir during the earthquake of 1965 (Folchi, 2003). As a result of this catastrophic event, approximately 6,500,000 m³ of water-saturated mining wastes were dumped into the El Cobre Creek (Figure 3). These mining wastes have affected an area approximately 8 km long that extended to the town of El Melón (Folchi, 2003).

Along the El Litre Creek, the total copper concentrations were greater than those that were observed along the El Carretón Creek, despite the fact that mining activities have been virtually absent along both creeks (Figure 3). Most likely, the higher copper concentrations along the former creek were also a result of the 1965 earthquake.

Catemu – Llay-Llay sampling area

In the Catemu – Llay-Llay sampling area (Figure 4), the total copper concentrations ranged from 80-250 mg kg⁻¹. One exception was a sample collected near the El Sauce mine dump with a measured copper concentration of 750 mg kg⁻¹ (Figure 4, Table 1).

Catemu – Panquehue sampling area

In the Catemu – Panquehue sampling area (Figure 4), the total copper concentrations were similar to those in the Quillota sampling area, in agreement with the virtual absence of mining activities in both areas

(Table 2). Likewise, the spatial distribution of copper was relatively homogeneous, exhibiting coefficients of variation of 24-25% (Table 1).

Catemu – Ñilhue sampling area

The relatively high copper concentrations near Ñilhue (Table 1, Figure 4) most likely resulted from an old smelter that was established in this locality in 1841 (Huidobro, 1861; Folchi, 2001). A separate and more recent La Poza smelter at Ñilhue was created at the beginning of the 20th century (Folchi, 2006). Neither of the smelters has remained, but two smelter slag dumps near Ñilhue serve as evidence for the former smelting activities.

The relatively high copper concentrations along the Catemu Creek probably resulted from the erosion of material from the mine and smelter slag dumps that are located in the upstream part of the creek. In agreement with this postulation, the highest measured copper concentration (2400 mg kg⁻¹) was observed near the smelter slag dump. The copper concentrations near the mine dump to the west of Catemu were also relatively high (Figure 4).

Catemu – Chagres sampling area

In the Catemu – Chagres sampling area, the highest (up to 900 mg kg⁻¹) total copper concentrations were observed to the northeast and to the southwest of the smelter (Table 1, Figure 4). This corresponds with the predominant northeast and southwest wind directions in the area (Empresa Melón, 2005). In addition, some erosion of the smelter slag that was deposited near the river could have contributed to the high copper concentrations to the southwest of the smelter, downstream from the Aconcagua River.

In the Catemu – Chagres sampling area, the spatial distribution of copper was very heterogeneous,

exhibiting a coefficient of variation of 223 % (Table 1), which is indicative of anthropogenic impacts. If the copper concentrations in the soils of the Catemu – Chagres sampling area would have been controlled by geological processes, we would expect copper concentrations to not exceed those measured in the Catemu – Panquehue sampling area that is located upstream and nearby. This, however, was not the pattern revealed by our data (Table 1, Figure 4).

We therefore concluded that the relatively high and heterogeneously-distributed copper concentrations in the Catemu – Chagres sampling area most likely resulted from the smelting activities. The smelter at Chagres was constructed in 1927. However, effective actions to mitigate its atmospheric emissions were not performed until 1991 (Folchi, 2006).

Putaendo sampling area

In the Putaendo sampling area (Figure 5), the total copper concentrations were similar to those in Quilota (Figure 2). We therefore concluded that small-scale mining in the Putaendo sampling area (Table 2) had a minor impact on the soil copper concentrations. Sánchez and Enríquez (1996) similarly reported the limited environmental impacts of small-scale mining on soils and water quality.

Los Andes sampling area

In the northeastern part of the Los Andes sampling area, along the El Cobre Creek, the relatively high copper concentrations most likely resulted from the activities of two small-scale mines (Figure 6). However, the copper concentrations in this location were considerably greater than those in the Putaendo sampling area, where a great number of small-scale mines

are present (Figure 5, Table 2). This difference was probably due to the distance between the sampling locations and the mining activities. In the Putaendo sampling area, mines were situated at relatively large distances from the study area boundary, which corresponded to landforms with slopes of less than 15%. In contrast, in the Los Andes sampling areas, mines were situated in close proximity to the study area boundary and the sampling locations.

In the eastern part of the Los Andes sampling area, where the confluence of the Juncal and Colorado Rivers gives rise to the Aconcagua River (Figures 6 and 7), total copper concentrations differed by an order of magnitude in locations in close proximity (Table 1). The samples collected along the Colorado River, where mining activities are absent, exhibited considerably smaller copper concentrations than the samples collected along the Aconcagua River, downstream of the confluence of the Juncal and Colorado Rivers. In the latter samples, the relatively high copper concentrations suggested that they resulted from the large-scale mining activities of the Andina complex located upstream along the Blanco River, the main tributary of the Juncal River (Figure 7, Table 2). Total decontamination of the mining effluents of the Andina complex did not occur until the construction of a decontamination plant in 2001 (CODELCO División Andina, 2001). Additional studies are necessary to establish a pattern for the soil copper distributions in the region of the Colorado and Juncal River confluence and the effects of mining activities.

In other locations along the Aconcagua River in the Los Andes sampling area (Figure 6, Table 1), the relatively high concentrations could be due either to the natural abundance of copper in the soil or to contamination from upstream mining industries.

4. Conclusions

There were no statistically significant differences between the sampling areas with regard to organic matter content and copper concentrations. However, the sampling areas differed significantly with regard to pH.

In the areas where mining activities were absent, the total copper concentrations ranged from 70-160 mg kg⁻¹. High copper concentrations (above 700 mg kg⁻¹, with a maximum of 4000 mg kg⁻¹) were generally observed near mining activities or in areas where mining activities were located nearby and upstream. In these areas, the copper concentrations differed by an order of magnitude in nearby locations.

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