PRELIMINARY PHYSICAL CHEMICAL CHARACTERIZATION OF RIVER WATERS AND SEDIMENTS AFFECTED BY COPPER MINING ACTIVITY IN CENTRAL CHILE. APPLICATION OF MULTIVARIATE ANALYSIS

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ABSTRACT

The concentration of trace elements and other analytes of environmental interest was determined in waters and sediments of the Coya and Cachapoal rivers (VI Region, Central Chile), which corresponds to a location highly polluted by copper mining activity.

Analysis showed the highest pollution at the sampling station closest to the copper smelter (Caletones), then pollutant concentrations decrease at sites far away from this source.

The statistical correlation between the different variables determined in waters and sediments was carried out through a principal components analysis (PCA). It was observed that the parameters fell into three groups: (a) analytes present in waters and sediments which come from the mining wastes (b) analytes of lithogenic character present in waters plus alkaline and alkaline earth metals plus organic matter present in sediments and waters, and (c) lithogenic elements present in sediments. On the other hand, by using cluster analysis (CA), it was possible to group the different sampling stations according to their extent of pollution.

INTRODUCTION

The contamination of rivers by trace elements coming from mining activity is today considered a global problem of international concern because the ecosystems located along the river can be damaged.[1]

The impact of this kind of contamination depends on a number of factors including nature of the mining extraction process, nature of the ores, efforts in the control of contamination, and also on environmental factors. It is well-known that physical-chemical factors such as pH, redox potential and nature and concentration of organic matter, control the mobility and availability of trace elements. [2-4]

Sediment analysis has been widely used as an environmental indicator to assess the extent of contamination in an aquatic system. Its ability to identify pollution sources is widely recognized.[5-10] Therefore, in order to understand the environmental behavior of elements including pollutants and taking into account that sediments are in continuous interaction with the liquid phase, it is more convenient to combine both water and sediment analysis. [8-10]

Chile has experienced a dramatic increase in its mining activities in the past few years, bringing about investments and technological changes. Some of these changes, however, have had damaging effects on the environment. Mining processes produce a considerable amount of wastes part of which is dispersed in the air, water and soils. The surroundings of the Caletones smelter, located in the VI region of the country, in central Chile, is also impacted by this kind of mining activity. It has been demonstrated that heavy metals are emitted from this source.[9,10] In that area, the Cachapoal River has received for years the effluent from mining activities, affecting agricultural and probably aquatic life close to the outlet of the Cachapoal River into the Pacific Ocean. Taking these antecedents into account, the biggest mining company in Chile is taking steps to ensure that copper becomes an environmentally sustainable element over time and will contribute to reduce any possible negative effects of its production and use throughout its life cycle.[9,11]

It has been internationally recognized that in Chile there is lack of scientific information related to the flow and mobility of contaminants in aquatic ecosystems[12]. This is particularly true of aquatic systems of the VI Region in Central Chile, which are affected by mining activities. In previous studies,[9,10] it was found that arsenic was mainly present as As(V) in both water and sediment, and organic arsenic species were not detected. The presence of high concentrations of arsenic and copper found in all the samples under analysis suggests a real impact of the mining activity over the region. The presence of arsenic in water and in sediments probably resulted from an acid drainage, because pollution clearly diminished with the distance from the source. In the case of soils, they can be impacted by irrigation with river water. However, the high concentration values determined at sites far from the source suggest that soil pollution is more related to air particles deposited in soils. At the most impacted sites, most arsenic is immobilized as a form of As (V).[9]

In this study, the preliminary physical chemical characterization of water and sediment samples collected at different points of the Coya and Cachapoal rivers has been carried out. The main objectives of this study were to determine the element concentration in waters and sediments and to establish the extent of contamination in this aquatic system at different distances from the main pollution source (Caletones smelter). Further, statistical data treatment was carried out by principal component analysis (PCA) and cluster analysis (CA) in order to reduce the amount of physical chemical variables for correlation and grouping of the sampling points according their pollution extent.

EXPERIMENTAL

Reagents

All chemical used were of analytical grade. De-ionized water (NANOpure ultrapure water system, Barnstead) was used throughout. Working solutions of different concentrations of arsenic species were prepared from 1000 mg L^{-1} standard solutions. As(III) standard solution was prepared by dissolving extra pure reagent As_2O_3 (Aldrich, Milwaukee, WI, USA) in 0.1 mol L^{-1} NaOH solution (Merck). As(V) standard solution was from WAKO pure Chemical industries, Japan. Monomethylarsonic acid (MMAA) and Dimethylarsinic acid (DMAA) standard solutions were prepared by dissolving the pure reagents (Tri Chemical Laboratory Inc., Japan). A 5 % sodium tetrahydroborate (Merck) solution was prepared in 0.25 % NaOH just before use.

Multielement standards QCS-26 and ICP-200.7-5 (High Purity Standard, USA) were used for ICP measurements of total concentration elements (As, Cu, Zn, Pb, P, Fe, Al, Si, Mg, Ca, Na, K). An AccuStandard, Inc. multistandard was used for sulphate and nitrate determination.

A Na_2CO_3/$NaHCO_3$ (3.5 mmol/L /1.0 mmol/L) buffer system was used as eluting agent in ion chromatography.

Nitric acid 65%, Suprapur® (Merck) y HF 40% (Merck) was used for sediment microwave digestion. Solutions of 1 mol/l $K_2Cr_2O_7$ (Merck), 5 mol/l $FeSO_4 \times 7H_2O$ (Mallinckrodt Analytical Reagent) and ferroin (Sigma-Aldrich Co.) were used for organic matter determination in sediments.

Water samples for analysis of trace elements were preserved al pH<2 by adding drops of HNO_3 (Merck) and H_2SO_4 (Merck) for determination of Total organic carbon (TOC).

Instrumental

An Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) Perkin Elmer Optima 3300 XL was used to determine the total element concentrations in water and sediment samples. The manifold used for arsenic speciation has been described elsewhere.[9,10] It basically consists of a hydride generation (HG) system connected to a Cold-trap unit (U-tube half-packed with Chromosorb W AW-DWCS 60/80 mesh OV-3 (15 %) (Supelco, Bellfonte, PA)) and an ICP-OES.

A Dionex 120 ion chromatograph with an AS 14 analytical column and an AG 14 pre-column was used for determination of nitrate and sulphate in water samples. In situ measurements of pH, Eh (redox), and EC (electrical conductivity) were carried out at each sampling point by using a portable water quality multiprobe (Hydrolab) that had been calibrated on the sampling day.

Sampling

The Coya and Cachapoal rivers were considered in this study. Figure 1 shows the sampling area. It comprises a wide area of Central Chile (VI Region) with intense agricultural and mining activity. The sampling program considered

sample collection mainly from locations near the Caletones smelter on the NE to sectors next to Rapel Lake, located west of Rancagua City. Three sampling periods were considered: April 2003, April 2004 (autumn) and August 2004 (winter). Sampling station Nº 9 (Tinguiririca river) was selected for comparison and assessment of background level in this area because it is not affected by heavy metal pollution.
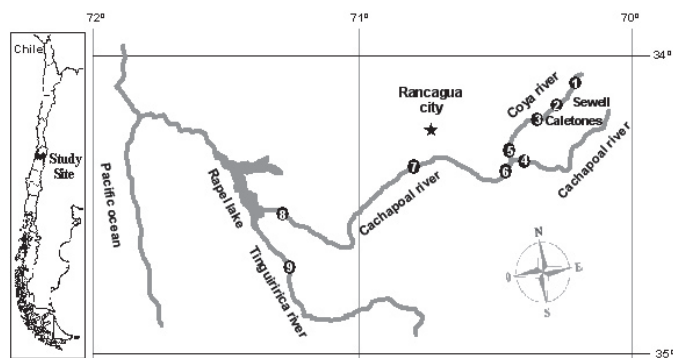
Figure 1. Location map of VI Region, Chile, indicating the sample stations under study.

Surface water samples were taken from both rivers. All water samples were collected in clean polyethylene bottles, filtered through 0.45 um, kept at 4°C and frozen on arrival at the laboratory until analysis. One additional water sample, filtered and preserved with nitric acid (pH <2), was taken at each sampling point for total element determination. Samples of sediment were also taken at each point.

Samples of loose surface sediment were collected in polyethylene bottles, using a plastic trowel. All sediment samples were air dried, ground and sieved (0.6 mm).

Procedures

Total element determination was carried out by ICP-OES, following the US-EPA 6010B method.[13] The sediment samples (0.3 g) were previously digested in a microwave oven Millestone mls 1200 mega following the US-EPA 3051 method.[14]

Arsenic speciation was carried out by hydride generation coupled to cold trap and ICP-OES.[9,10] In the case of sediments, 5-g samples were extracted with 25 mL of 1 mol L^{-1} HCl by shaking mechanically at 30 °C and 200 rpm for 1h. Speciation was carried out in the extract.[9]

Determination of organic matter in sediments was carried out by Walkley-Black method.[15] Nitrite and sulphate were determined by ion chromatography [16] and Total organic carbon was measured by Combustion-Infrared Method. [16]

Statistical analysis

In this study, the statistical analysis of the results was based on Principal Component Analysis (PCA)[17,18] and Cluster Analysis (CA)[17,19].

PCA and CA were carried out by using the statistical package Statgraphic Plus v. 5.1. The experimental data were standardized before the chemometrical analysis by subtracting their mean values and dividing them by their standard deviations.

The most relevant physico-chemical variables in both filtered waters and superficial sediments were considered. In addition, data standardization of each variable was done prior to statistical analysis because the concentration orders among the elements and the parameters differed greatly and statistical results would be highly biased by elements with high concentration.[8]

CA was performed from the original data in order to reduce the variant biases. The Furthest Neighbor method was applied for grouping of the different variables, and dissimilarity was defined by City-Block distance.

RESULTS AND DISCUSSION

Water

Determination of physical and chemical parameters in water was carried out at the nine sampling stations. As can be seen in Table 1, the lowest pH value and the highest values of both electric conductivity (EC) and redox potential (Eh) were measured at sampling station Nº 2 (Coya River between Sewell and Caletones). This sampling point also showed the highest concentrations

of trace elements (such as Cu, Fe, and As), anions and TOC, which indicates that the main discards of mining waste into the Coya river occurred between sampling stations 1 and 2.

On the other hand, it can be observed that downstream of sampling point 2 of the Coya River, concentrations of all parameters decreased due to dilution and sorption on the surface of sediments. After the Coya river joins the Cachapoal River, the concentrations of these parameters decreased to a higher extent, reaching the background level, defined by point 9, at sampling station 8.

Due to the available information, special care must be taken if some dredge or sediment removal occurs, because the sulfides and some metals retained in this river fraction can be released, contaminating these aquatic systems even more.[20]

On the contrary, the concentrations of P, Al, and Si in water remain almost constant at all sampling points (Coya – Cachapoal), which is consistent with the lithogenic nature of these elements. Contrary to Coya and Cachapoal rivers, Tinguiririca river (point 9) showed lower concentration of Fe, Al, Si, SO$_4^{2-}$ and lower Eh and EC, which can be attributed to the different mineral composition of its sediments.

Regarding the seasonal effect, a slight decrease was observed in trace element concentrations in water in August 2003 (spring) compared with April, which is consistent with the increment in the flow rate of the rivers under study in this period. However, only in this period methylated arsenic species were determined, which is in agreement with the slight increment in TOC concentration making microbiological activity possible.[21]

Sediment

The determination of chemical parameters in sediment was carried out at the nine sampling stations (Table 2). Similar to the observations in water analysis, higher concentrations of trace elements, including arsenic species, and organic matter were determined at sampling station 2. Downstream of this point the concentrations decreased to reach almost the background level at sampling station 8. In contrast, sampling stations 1-8 showed similar concentrations of P, Al, Si, Ca, Mg, Na and K among them. However a comparison with sampling point 9 (Tinguiririca River) indicates that concentrations of Fe, Al and Si were lower in the latter case, possibly due to the different composition of the parenteral material of both basins.

Seasonal variations were lower in sediments than in water, which can be explained because dilution affects sediments to a lower extent.

Multivariate analysis

The procedure of multivariate analysis was based on the observations obtained in relation to several variables for a number of samples (also called eigenvectors). Multivariate methods to analyze environmental data constitute an increasingly important part of statistics, because they allow an easier interpretation of the results.[22-24]

Principal component analysis (PCA)

PCA was applied in order to obtain a statistical correlation among the different components of the environmental matrices analyzed (river waters and sediments). The application of PCA allowed reducing the number of the variables in a few components with minimum loss of information, which was obtained by the linear combination of all the variables in consideration. The number of the main components was obtained on the basis of the sum of the eigenvectors (eigenvalue) being greater than 80% of the total variability.

The application of PCA to the set of variables determined in filtered waters as well as in surface sediments indicated that these 39 selected variables were represented by 3 new variables or principal components. These 3 new components account for near 87% of the total variance in the data set. Therefore, three vectors were used for statistical analysis. The eigenvectors and eigenvalues obtained in this analysis are shown in Table 3. In order to achieve the association of the variables to each principal component, the corresponding weights (eigenvectors) in the scores matrix were analyzed, and the highest weight observed allowed to associate the corresponding variable to that component. The eigenvectors classified the 39 physico-chemical variables (elements, compounds and field parameters) into the following three components:

• Component 1: Total As and its species in river waters and sediments, heavy metals generated by mining activities in river waters and sediments, field parameters (pH, Eh, EC), and geological components present in waters.

• Component 2: Lithogenic elements in river waters, alkaline and alkaline earth metals present in sediments, and organic compounds in water and sediments.

Table 1. Preliminary physico-chemical characterization of the river waters.

Sample Station	Waters																					
	As	Cu	Zn	Pb	P	As(III)	As(V)	MMA	DMA	Fe	Al	Si	Mg	Ca	Na	K	SO_4^{2-}	NO_3^-	TOC	pH	Eh	EC
	--------------------------------µg/l--------------------------------									--------------------------------mg/l--------------------------------											mV	µS/cm
S. 4 Ap 2003	27	58	57	1.5	46	2.5	22	<DL	<DL	0.91	60	134	5.9	61	18	2.9	116	0.91	<DL	8.1	316	434
S. 5 Ap 2003	71	4860	477	4.7	47	13	54	<DL	<DL	6.2	61	135	24	155	24	8.4	456	3.4	<DL	6.5	422	995
S. 6 Ap 2003	57	2150	208	2.3	47	8.3	45	<DL	<DL	2.9	61	135	14	113	20	4.6	280	3.2	<DL	7.5	380	710
S. 1 Au 2003	26	18	5.2	2.4	41	2.5	23	<DL	<DL	1.0	58	130	6.8	97	14	6.1	182	1.5	<DL	7	337	403
S. 2 Au 2003	204	24400	1340	40	41	73	103	3.2	1.6	33	60	132	33	194	24	8.7	553	5.7	9.3	5.7	496	1530
S. 3 Au 2003	110	6260	785	32	41	31	64	2.0	1.3	22	58	125	25	144	23	7.7	443	3.8	8.4	6.2	465	961
S. 4 Au 2003	22	46	45	1.2	39	2.1	19	<DL	<DL	0.72	52	107	4.7	49	15	2.3	83	0.59	<DL	7.4	345	402
S. 5 Au 2003	40	2290	302	3.7	41	6.3	28	1.3	1.9	3.5	55	110	21	121	20	7.6	382	3.0	6.9	6.9	438	776
S. 6 Au 2003	31	1700	130	1.8	40	4.5	25	<DL	<DL	1.5	53	108	11	87	15	3.6	226	2.7	<DL	7.2	388	579
S. 7 Au 2003	22	116	14	<DL	38	2.6	19	<DL	<DL	1.2	53	105	11	85	13	3.4	109	2.8	<DL	7.3	362	510
S. 8 Au 2003	19	46	<DL	<DL	36	1.8	17	<DL	<DL	0.39	50	101	11	84	12	3.3	87	2.4	<DL	7.8	312	464
S. 9 Au 2003	18	12	<DL	<DL	45	1.6	16	<DL	<DL	0.01	1.5	15	7.2	42	16	7.4	61	3.4	4.2	8.5	290	339
S. 4 Ap 2004	29	61	58	1.5	47	2.9	24	<DL	<DL	0.94	62	138	6.1	62	19	2.9	121	0.94	<DL	8.3	310	446
S. 5 Ap 2004	65	4610	456	4.5	48	13	49	<DL	<DL	5.9	63	139	24	160	25	8.6	470	3.6	<DL	6.3	415	1010
S. 6 Ap 2004	56	2140	205	2.3	47	8.6	43	<DL	<DL	2.9	62	136	14	115	20	4.7	284	3.3	<DL	7.5	372	705
S. 8 Ap 2004	26	62	45	<DL	49	2.4	22	<DL	<DL	0.59	69	135	14	112	17	4.5	122	3.3	<DL	8.1	300	532

<DL: less than detection limit
Au: August; Ap: April

Table 2. Concentrations of heavy metals, major elements and organic matter percentage (O.M.) in river sediments.

Sample Station	Sediments																
	As	Cu	Zn	Pb	P	As(III)	As(V)	MMA	DMA	Fe	Al	Si	Mg	Ca	Na	K	O.M.
	--------------------------------mg/kg--------------------------------									--------------------g/kg--------------------							%
S. 4 Ap 2003	10	60	64	12	724	0.24	2.8	<DL	<DL	15	77	188	16	30	21	17	434
S. 5 Ap 2003	135	5050	244	48	724	11	34	<DL	<DL	32	77	186	16	31	21	17	995
S. 6 Ap 2003	73	2550	160	36	713	3.8	18	<DL	<DL	32	77	185	16	30	21	16	710
S. 1 Au 2003	10	22	5.9	11	723	0.28	2.9	<DL	<DL	17	86	200	15	29	20	16	403
S. 2 Au 2003	281	24900	768	118	721	46	61	5.2	3.0	55	86	203	18	31	21	17	1530
S. 3 Au 2003	190	12400	431	82	722	21	42	4.0	2.7	44	86	198	17	31	20	17	961
S. 4 Au 2003	8.3	50	53	9.6	719	0.22	2.4	<DL	<DL	13	76	187	15	29	21	16	402
S. 5 Au 2003	111	4140	200	39	721	6.9	22	3.8	5.5	26	76	185	16	30	20	17	776
S. 6 Au 2003	60	2110	131	29	711	3.1	16	0.44	0.52	26	76	184	16	29	20	16	579
S. 7 Au 2003	35	281	49	4.8	710	1.1	9.9	<DL	<DL	14	78	182	15	29	20	15	510
S. 8 Au 2003	15	49	7.7	<DL	708	0.31	4.4	<DL	<DL	10	80	180	15	29	20	15	464
S. 9 Au 2003	7.6	16	<DL	<DL	845	0.13	2.2	<DL	<DL	3.7	2.6	28.4	15	29	20	17	339
S. 4 Ap 2004	11	63	67	13	741	0.32	3.1	<DL	<DL	16	79	193	16	31	22	17	446
S. 5 Ap 2004	129	4820	235	46	743	11	32	<DL	<DL	31	79	191	17	32	22	18	1010
S. 6 Ap 2004	72	2520	158	35	719	3.9	18	<DL	<DL	32	77	187	17	30	21	17	705
S. 8 Ap 2004	20	65	10	<DL	825	0.42	5.8	<DL	<DL	13	100	225	19	36	25	20	532

<DL: less than detection limit
Au: August; Ap: April
As-speciation was carried out in 1 mol L^{-1} HCL extract.

• Component 3: Lithogenic elements present in sediments.
In other words, PCA indicated association between metallic and nonmetallic elements added to the rivers by the mining activity. In addition, the high concentration of polluting elements confirmed the established previously thought the measurement of field parameters (pH, Redox potential and conductivity) regarding to the contamination of the aquatic system. On the other hand, component 2 revealed that lythogenic elements present in high concentrations in river waters demonstrated similar behavior to that of lythogenic elements present in smaller concentration in sediments and with the organic compounds present in waters as well as in sediments. Finally,

component 3 revealed a correlation among the lythogenic elements present in high concentrations in sediments.

Cluster Analysis (CA)

The result of CA (cluster analysis) allowed to obtain data about the features of each sample of water and sediment, the different sampling stations included in this study being grouped in different conglomerates, based on their contamination extent, which is shown in a dendogram graph (Figure 2). The dendogram clearly revealed the formation of 2 groups:
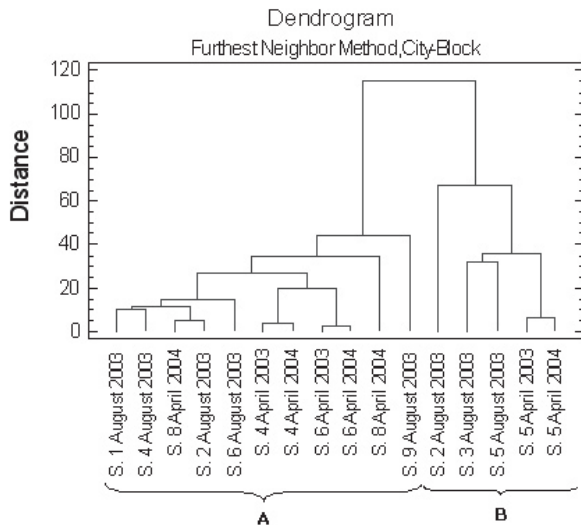
Figure 2: Dendrogram for cluster analysis obtained in the water-sediment system of the river. The dissimilarities are defined by City-Bock distance and the combination of clusters is based on Furthest Neighbor method.

A: Not impacted (stations Nº 1, 4 and 9) and not directly impacted by the mining spills (stations Nº 6, 7 and 8) sampling stations. In this latter group it was observed that sampling station Nº 8 (April of 2004) just as sampling station Nº 9 (August of the 2003), presented higher distances than the rest of the stations corresponding to group A.

In the case of sampling station Nº 8 (April, 2004), the greater City-Block distance may be attributed to the decrease in the flow rate of the Cachapoal river in April, 2004, in contrast with the flow rate observed during the other sampling periods, which favored a slight increase in lythogenic element concentration. On the other hand, the greater distance of sampling station Nº 9 (August of the 2003), corresponding to the Tinguiririca river (baseline), it attributed to the differences in mineral composition between the Tinguiririca and Cachapoal river basins.

B: Sampling stations directly impacted by copper mining activities of (stations Nº 2, 3 and 5). In this case it was observed that sampling station Nº 2 (August of the 2003) presented a higher City-Block distance than the other stations in group B, which was attributed to the greater concentrations of polluting elements added by mining spills as determined at this sampling station.

The statistical analyses were carried out considering the water and sediment samples independently, in order to make a comparison of the results with the system considered as a whole. Both PCA and CA provide similar results to the obtained when all experimental data were considered simultaneously. From an environmental point of view the later situation is more representative of an ecosystem because interactions between both compartments occur.

Information from the scores matrix PCA regarding from the components weights (Table 3) shows a similar grouping of the sampling sites obtained from the CA (Figure 2). As can be seen in Table 4, the sampling sites grouping as B in CA (Figure 2) showed the main weight in the component 3. Contrarily, the sampling sites grouping as A in CA (Figure 2) have the main weights in component 1 and 2 in PCA.

Table 3. Principal components analysis (loading matrix). Eigenvectors and eigenvalues on the correlation matrix of the concentrations and parameters determined in river water and sediments.

		Component 1	Component 2	Component 3
Waters	Al	0.0597	-0.3253	-0.2668
	As	0.1956	0.0041	0.0075
	As(III)	0.1898	0.0367	0.0121
	As(V)	0.1940	-0.0333	0.0027
	Ca	0.1797	-0.1236	-0.0132
	Cu	0.1867	0.0303	0.0167
	DMA	0.1547	0.1226	-0.0046
	EC	0.1959	-0.0484	0.0020
	Eh	0.1860	0.0319	-0.1097
	Fe	0.1928	0.0464	0.0027
	K	0.2038	0.0518	0.1421
	Mg	0.1897	-0.0441	0.0445
	MMA	0.1832	0.1024	0.0041
	Na	0.1537	-0.1304	0.1141
	Nitrate	0.1789	0.0262	0.1568
	P	-0.0041	-0.2806	0.2703
	Pb	0.1858	0.0625	-0.0038
	pH	-0.1832	-0.0047	0.1470
	Si	0.0671	-0.3229	-0.2507
	Sulphate	0.1840	-0.0537	-0.0188
	TOC	0.1553	0.1992	0.1151
	Zn	0.2008	0.0114	0.0146
Sediments	Al	0.0590	-0.2805	-0.2960
	As	0.2013	0.0108	-0.0010
	AsIII	0.1962	0.0360	0.0149
	AsV	0.1985	-0.0057	-0.0031
	Ca	0.0493	-0.3263	0.2318
	Cu	0.1968	0.0459	0.0089
	DMA	0.1300	0.1267	-0.0156
	Fe	0.1896	-0.0502	-0.0849
	K	0.0419	-0.3343	0.2662
	Mg	0.1154	-0.2687	0.1789
	MMA	0.1739	0.1193	-0.0070
	Na	-0.0083	-0.3534	0.2047
	O.M.	0.1735	0.1991	0.0714
	P	-0.0478	-0.0220	0.4697
	Pb	0.1992	0.0135	-0.0318
	Si	0.0605	-0.2858	-0.3014
	Zn	0.1997	0.0238	-0.0146
Eigenvalue		24.18	5.719	4.014
Proportion %		61.99	14.67	10.29
Cum. Proportion %		61.99	76.65	86.94

CONCLUSIONS

The VI Region of Chile has been impacted by liquid and air emissions from the copper mining process. The distribution of pollutants in waters and sediments of the Coya and Cachapoal rivers is controlled mainly by the distance from the pollutant source (copper smelter) and by the flow rate of the rivers. PCA indicated association among all heavy metals determined in the environmental matrices analyzed, revealing that their high concentrations are due to the discharge of liquid wastes to the Coya River. Further, CA correlated all sampling stations impacted by contamination resulting from the mining processes.

Table 4. Principal components analysis (score matrix).

	Component 1	Component 2	Component 3
S1 August 2003	0,2364	0,2696	0,0113
S2 August 2003	0,2107	-0,2994	0,3295
S3 August 2003	0,2197	-0,2822	-0,6070
S4 April 2003	0,2512	0,2515	0,0415
S4 April 2004	0,2517	0,2506	0,0452
S4 August 2003	0,2479	0,2559	0,0245
S5 April 2003	0,2403	-0,2651	0,2998
S5 April 2004	0,2429	-0,2616	0,2903
S5 August 2003	0,2520	-0,2427	-0,4929
S6 April 2003	0,2690	-0,2231	0,0972
S6 April 2004	0,2695	-0,2221	0,1084
S6 August 2003	0,2777	-0,2069	0,0292
S7 August 2003	0,2892	0,1750	-0,2720
S8 April 2004	0,2499	0,2519	0,0476
S8 August 2003	0,2484	0,2553	0,0288
S9 August 2003	0,2317	0,2603	0,0465
Eigenvalue	9.456	6.310	0.113
Proportion %	59.11	39.44	0.708
Cum. Proportion %	59.11	98.54	99.25

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