

ARSENIC SPECIATION IN ENVIRONMENTAL SAMPLES OF A MINING IMPACTED SECTOR OF CENTRAL CHILE

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ABSTRACT

The presence of high concentrations of arsenic and copper was determined in most of the environmental matrixes under study (river water, river sediments, and soils), which suggests a real impact of the copper mining activity throughout the region, specifically the surroundings of the Caletones smelter, in the VI Region of Chile. The presence of arsenic in water and sediments is probably due to acid drainage, because pollution clearly diminished with increasing distance from the source. In the case of soils, they may 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 airborne particles deposited in soil.

Arsenic speciation studies were carried out in river water samples and in edible tissues of fish (black kingclip, Chilean hake and croaker) and shellfish (clam, mussel and barnacle) samples, collected in the Pacific Ocean, close to the Cachapoal River outflow. In water samples, arsenic is mainly present as As(V); organic arsenic species (MMAA and DMAA) were not detected. In fish, around 80 % of arsenic is present as arsenobetaine.

Keywords: Arsenic speciation, River pollution, Water, Sediment, Soil.

INTRODUCTION

Chile has seen a dramatic increase in mining activities in the past few years, which has brought about investments and technological changes. Some of these changes, however, have had damaging effects on the environment. Mining processes produce a considerable amount of waste material, part of which is dispersed in the air, water and soil. This waste includes arsenic among other pollutants. The highest environmental arsenic concentrations have been found in the north of the country (1), and particularly the high level of arsenic in water has severely affected the health of the population (2). In central Chile, specifically the surroundings of the Caletones smelter, located in the country's VI Region, have also been impacted by this kind of mining activity. It has been shown that arsenic is one of the pollutants emitted by this source (3). In that area the Cachapoal River has received for years the effluent from mining activities, affecting agricultural and probably aquatic life in the Pacific Ocean, close to the Cachapoal River outflow. Taking this background into account, the biggest mining company in Chile is taking actions to ensure that copper becomes an environmentally sustainable element over time, and it will contribute to reduce any possible negative effects of copper production and use throughout the metal's life cycle.

The bioavailability of an element is largely related to its physico-chemical state, which also governs the solubility, mobility and toxicity of the element. Arsenic speciation studies are not only important to understand interaction and accumulation mechanisms, but also to determine mobility and bioavailability mechanisms related to this metalloid.

Arsenic speciation in water, considering inorganic and organic species, has been widely studied (4-6) in different countries. However, in Chile there are no studies in this respect in the VI Region. For arsenic speciation a number of analytical methods have been proposed (7-9),

based mainly on chromatographic separation and spectroscopic detection.

Arsenic forms present in soils and sediments depend on matrix component type, pH, and redox potential. In this context, several attempts have been made to separate the various forms of arsenic in soils and sediments, defining fractions such as soluble, exchangeable, bound to Fe-oxides, bound to organic matter, etc.

A direct correlation has been shown between the solubility of arsenic species and their biological effect on plants. For instance, soluble species in 1 mol L⁻¹ HCl have been considered bioavailable because a significant linear correlation between amount of arsenic extractable with 1 mol L⁻¹ HCl from soil and rice yield can be established (10). On the other hand, Kato et al. (11) have reported a poor correlation between total arsenic in soil and plant growth.

The aim of this study was to determine the arsenic pollution level in a mining-impacted region in central Chile. In this context, arsenic speciation studies were carried out in river water samples, and in fish and shellfish samples collected in the Pacific Ocean close to the Cachapoal River outflow. In addition, total and soluble arsenic levels were determined in sediment and soil samples from the region. A further purpose of the present study was also to validate a sensitive and selective analytical method for arsenic speciation in the region's water in order to determine the extent of pollution and mobility of this metalloid. The speciation method allows the determination of inorganic arsenic [As(III) and As(V)] and organic arsenic [monomethylarsinic acid (MMAA) and dimethylarsinic acid (DMAA)], which are relevant species from an environmental point of view, and it is based on the generation of the corresponding arsines, cold trap and continuous ICP-OES detection (HG-Cold trap-ICP). The method corresponds to a modified version of an earlier method reported by Edmonds and Francesconi (12) in which ICP-OES is used instead of atomic absorption spectroscopy, improving in this way the sensitivity of the method.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade. Deionized water (NANOpure ultrapure water system, Barnstead, Dubuque, IA, USA) was used throughout. Working solutions at 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 As₂O₃ (Merck). As(V) standard solution was from WAKO Pure Chemical Industries Ltd., Japan. MMAA and DMAA standard solutions were prepared by dissolving the pure reagents (Tri Chemical Laboratory Inc., Japan). A 5% w/v sodium tetrahydroborate (Merck) solution in 0.25% w/v NaOH was prepared just before use. Solutions of 0.3 and 1 mol L⁻¹ HCl were prepared from 37% HCl (Merck) in deionized water. A 0.38 mol L⁻¹ citric acid/citrate buffer (pH 6.0) was prepared from monohydrated citric acid (Merck), and the desired pH was reached by adding 5 mol L⁻¹ NaOH. A 0.1 mol L⁻¹ L-cysteine (Merck) solution was used in order to minimize heavy metal interference (13) in the hydride generation process.

Instrumental

A Perkin Elmer Optima 3300 XL Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used to determine total arsenic and copper in water, sediment, and soil samples. The same instrument was used as the detector for arsenic speciation studies in water samples.

The manifold for speciation (Figure 1) consisted of a hydride generation system containing a 30 mL Pyrex glass reaction vessel that was connected through PTFE tubes to a water trap and a CO₂ trap, and then connected to a 40-cm quartz U tube half-packed with Chomosorb W AW-DMCS 60/80 mesh OV-3 (15%) (Supelco, Bellefonte, PA). The solid support was secured with DCMS-treated glass wool plugs. The U tube was wrapped with 1.5 m of 1.6 Ω ft⁻¹ resistance wire connected to a variable output transformer. The quartz U tube was connected to the ICP-OES instruments through a PTFE line.

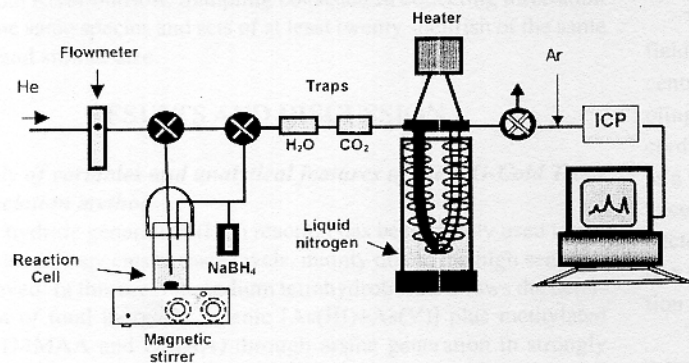


Fig. 1. Manifold for arsenic speciation.

Arsenic extractions from soils and sediment were carried out by using a Heidolph promax 2020 reciprocal shaker.

In situ measurements of pH, Eh, temperature, oxygen, and electrical conductivity were determined at each sampling point by using a portable water quality multiprobe (Hydrolab) that had been calibrated on the sampling day.

Speciation in fish and shellfish was carried out in Japan by HPLC-ICP-MS according to a previously reported procedure (14). The HPLC

pump was a LC410 BIO (Perkin Elmer) and the ICP-MS was a PMS100 instrument (Yokogawa).

Procedure

Total arsenic and copper concentrations were determined in water, sediment and soil samples by ICP-OES, following the US-EPA 6010B method (15). Water samples were directly analyzed by ICP-OES. Soil and sediment (0.3 g) samples were previously digested in a Milestone mls 1200 mega oven following the US-EPA 3051 method (16).

To determine the mobile fraction of arsenic in some of the soil and sediment matrixes, 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. Total soluble arsenic was determined in the extract.

Study of variables and speciation procedure

The variables associated with the hydride generation process were optimized by the univariate method. The variables were studied in the following ranges: HCl concentration: 0.03–0.45 mol L⁻¹; NaBH₄ concentration: 1–5%; preconcentration time: 1–5 min; helium flow rate: 1.0–10 mL min⁻¹; argon flow rate: 0.5–1 mL min⁻¹.

Hydride generation at pH 1.0: 5 mL of water sample (or 1 mol L⁻¹ HCl extract), 5 mL of 0.3 mol L⁻¹ HCl (or deionized water), and 1 mL of L-cysteine solution were placed in the reaction vessel, and deionized water was added to reach a final volume of 20 mL. This mixture had a final pH about 1.0.

Hydride generation at pH 6.0: 5 mL of water sample (or 1 mol L⁻¹ HCl extract), 10 mL of citric acid/citrate buffer, and 1 mL of L-cysteine solution were placed in the reaction vessel, and deionized water was added to reach a final volume of 20 mL. This mixture had a final pH about 6.0.

At either pH value, thorough mixing of the content of the reaction vessel by bubbling helium at 9 mL min⁻¹ was followed by injection of 1 mL of a 5% w/v solution of NaBH₄ in 0.25% w/v NaOH into the vessel. At this point the He-flow was directed to the U tube, which was immersed in a Dewar flask containing liquid nitrogen. After 3 min of cold trapped preconcentration, the arsines were released from the U tube by removing this from the liquid nitrogen and applying heat. The helium flow containing the arsines merged with an argon flow (0.6 mL min⁻¹) which carried them to the ICP-OES. The signals were collected and treated by an ICP Crom 3 software developed by Perkin Elmer Chile.

Edible tissues of fish and shellfish samples (17) were lyophilized and weighed (0.1 g), then they were extracted five times with 5 mL of methanol/water (1:1, v/v), and the extracts were combined, evaporated, and dissolved in 5 mL of water. After filtration, an aliquot was injected into the HPLC – ICP-MS system.

Sampling

Figure 2 shows the sampling area. It comprises a wide area of Central Chile with intense agricultural and mining activities. The sampling program considered collection of samples mainly from locations near the Calientes smelter on the NE to sectors next to Lake Rapel, located west of the city of Rancagua. Two sampling periods were considered: November 2001 (Spring) and March 2002 (Summer).

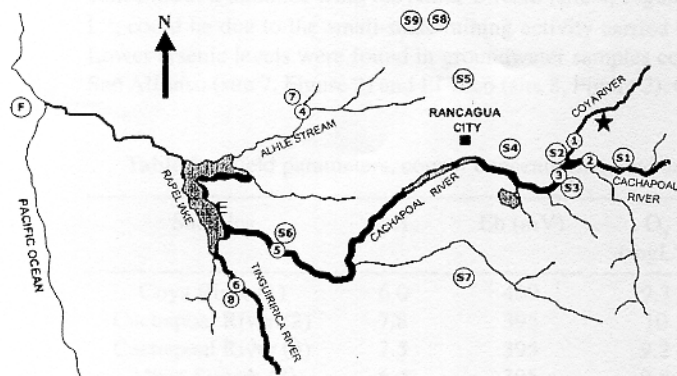


Fig. 2. Map of VI Region, Chile, showing the aquatic and terrestrial ecosystem studied; major city (Rancagua), sampling sites, and copper smelter (Caletones) are indicated with square, circles and star, respectively. S: soil; F: fish and shellfish

Surface water samples were taken from different rivers and a stream. Groundwater samples were also considered at some specific points. All water samples were collected in clean polyethylene bottles, filtered through 0.45 μm , kept at 4 $^{\circ}\text{C}$ and frozen upon arrival at the laboratory until analysis. Two additional water samples were taken at each sampling point. Only one of them was filtered and both were preserved with nitric acid (pH < 2.0). Samples of sediment and soils were also taken at each point in November 2001.

Samples of loose surface sediment were collected in polyethylene bottles, using a plastic trowel. All sediment samples were air dried, ground, and sifted (0.6 mm). Surface (0-10 cm) and subsurface (10-50 cm) composed soil samples were collected in polyethylene bags using an auger. The samples were air dried, ground, and sifted (2 mm).

Fish and shellfish were collected in the Pacific Ocean, close to the Cachapoal River outflow. Sampling consisted in collecting three adult fish of the same species and sets of at least twenty shellfish of the same species and similar size.

RESULTS AND DISCUSSION

Study of variables and analytical features of the HG-Cold Trap-ICP speciation method

The hydride generation (HG) reaction has been widely used to determine arsenic species at trace levels, mainly due to the high sensitivity achieved. In this method, sodium tetrahydroborate allows the determination of total inorganic arsenic [As(III)+As(V)] plus methylated species (MMAA and DMAA) through arsine generation in strongly acidic media (pH 1.0), while arsenite is determined at pH 6.0 (18).

The selected values for the variables under consideration were 0,3 mol L⁻¹ HCl, 5% w/v NaBH₄, 3 min of preconcentration time, 9 mL min⁻¹ helium, and 0.6 mL min⁻¹ argon flow rates. Figure 3 shows the chromatograms obtained under optimum conditions at pH 1.0 and 6.0.

Under the selected conditions the method has good analytical features. Detection limits and repeatability (% RSD) were the following: As(III): 0.021 $\mu\text{g L}^{-1}$ and 1.52%; As(V): 0.041 $\mu\text{g L}^{-1}$ and 3.77%; MMAA: 0.096 $\mu\text{g L}^{-1}$ and 2.32%; DMAA: 0.218 $\mu\text{g L}^{-1}$ and 3.87%.

Unfortunately, there are no certified reference materials for arsenic speciation in environmental samples; thus, recovery studies were made in spiked river water samples, showing a high level of accuracy (between 97.2 and 103%). In order to validate the speciation method, NIES

No. 18 Human Urine certified reference material was used, in which the concentration of DMA is certified (36 \pm 9 mg As L⁻¹). The concentration obtained for this species was 31 \pm 8 mg As L⁻¹, which indicates good performance of the method.

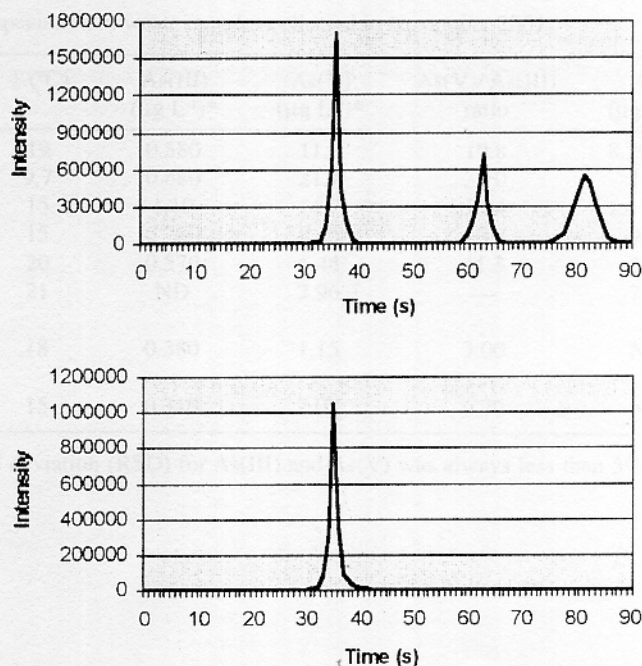


Fig. 3. Analytical signals for arsenic speciation at (a) pH 1.0 and (b) pH 6.0.

Water samples

The water samples at all sampling points were characterized in the field by determining pH, redox potential (Eh), temperature, and O₂ concentration. These results are shown in Tables 1 and 2 for the two sampling periods. As can be seen, the pH values ranged from 6 to 8. According to the determined Eh values and O₂ concentration, surface water as a whole corresponds to an oxidizing environment favoring the presence of arsenic in its maximum oxidation state [As(V)]. As can be expected, groundwater samples (Table 1) showed a relatively lower redox potential and oxygen level, and a lower As(V)/As(III) concentration ratio.

The temperature of the water ranged from 9.7 to 21 $^{\circ}\text{C}$. It is interesting to point out that the samples from the Coya (site 1, Figure 2) and Cachapoal (site 2, Figure 2) Rivers were collected almost simultaneously before the confluence of both rivers. However, there was a temperature difference of 9 $^{\circ}\text{C}$ between them, which could be indicating the release of an acid mine drainage into the Coya River. This is consistent with the difference in pH and the high level of copper determined in the Coya River (8.29 mg L⁻¹).

Table 1 shows the first results obtained in November 2001. The samples obtained from both the Coya (site 1, Figure 2) and Cachapoal (sites 2 and 3, Figure 2) Rivers showed the highest levels of arsenic, over 12 $\mu\text{g L}^{-1}$. These sampling sites are the closest to the smelter, the main source of arsenic pollution. The other sampling sites, farther from

the smelter, showed lower arsenic concentrations. The total arsenic concentration obtained from the Alhué Stream (site 4, Figure 2), $9 \mu\text{g L}^{-1}$, could be due to the small-scale mining activity carried out there. Lower arsenic levels were found in groundwater samples collected at San Alfonso (site 7, Figure 2) and El Toco (site 8, Figure 2). Consider-

ing the background levels of arsenic in various rivers of the world (19) (average $0.83 \mu\text{g L}^{-1}$, range $0.13 - 2.1 \mu\text{g L}^{-1}$), the aquatic system under study shows clear signs of arsenic pollution, a situation which is more severe in the Coya and Cachapoal Rivers, and it is also accompanied by significant copper pollution.

Table 1. Field parameters, copper concentration, and arsenic speciation in water samples collected in November 2001.

Samples	pH	Eh (mV)	O ₂ (mg L ⁻¹)	T (°C)	As(III) ($\mu\text{g L}^{-1}$)*	As(V) ($\mu\text{g L}^{-1}$)*	As(V)/As(III) ratio	Cu ($\mu\text{g L}^{-1}$)*
Coya River (1)	6.0	469	9.3	19	0.580	11.5	19.8	8.29×10^3
Cachapoal River (2)	7.8	395	10	9.7	0.680	21.1	31.0	10.7
Cachapoal River (3)	7.5	395	9.2	15	1.10	14.7	13.4	1.41×10^3
Alhué Stream (4)	6.4	395	9.8	15	0.780	8.45	10.8	9.38
Cachapoal River (5)	8.2	342	10	20	0.570	6.44	11.3	60.2
Tinguiririca River (6)	8.1	330	9.8	21	ND	2.96	—	7.18
San Alfonso (ground-water) (7)	7.0	354	12	18	0.380	1.15	3.00	NM
El Toco (ground-water)(8)	6.2	366	4.0	15	0.310	2.08	6.70	NM

* Mean of three independent determinations. Relative standard deviation (RSD) for As(III) and As(V) was always less than 5%, RSD for copper determination was less than 2%.

Numbers in brackets refer to sampling sites in Figure 2.

ND: not detected

NM: not measured

In all cases the predominant species corresponded to As(V), which was in agreement with the field parameters determined. Organic arsenic species (MMAA and DMAA) were not detected at any of the sampling sites.

The flow rate of the rivers decreased considerably in summertime (March, 2002). Consequently, an increase was seen in this period in the measured arsenic concentration (Table 2). At all the sampling locations, except Coya (site 1, Figure 2), the total arsenic concentration determined in March 2002 was 2 to 3 times higher than that of November 2001. However, in the Coya River the arsenic concentration of 354

$\mu\text{g L}^{-1}$ found in March was almost 30 times higher than that determined in November and this cannot be explained only by the decline in the river's flow rate. In this context, a clear additional contribution of arsenic pollution has to occur around this period.

On the other hand, when total arsenic was determined in the Coya River (site 1, Figure 2) but in unfiltered water samples, the arsenic concentrations found in November increased from $12.08 \mu\text{g L}^{-1}$ to $55.0 \mu\text{g L}^{-1}$. According to this, probably the main mobilization of arsenic from the Coya River to the Cachapoal River is via suspended particles, similar to what Chunguo and Zihui (20) found in the Xiangjiang River in China.

Table 2. Field parameters and total arsenic concentration in water samples collected in March 2002.

Samples	pH	Eh (mV)	O ₂ (mg L ⁻¹)	T (°C)	Total As ($\mu\text{g L}^{-1}$)*	As March/As Nov ratio
Coya River (1)	6.0	472	9.0	18	354	29
Cachapoal River (2)	7.0	354	12	9.0	65.5	3.0
Cachapoal River (3)	7.0	384	11	14	35.1	2.2
Alhué Stream (4)	6.8	388	9.8	14	20.1	2.1
Cachapoal River (5)	8.1	328	9.8	21	16.6	2.3
Tinguiririca River (6)	7.9	318	9.5	21	7.20	2.4

* Mean of three independent determinations. RSD was less than 8 %

Numbers in brackets refer to sampling sites in Figure 2.

Sediment samples

Sediment samples were taken in November 2001. Table 3 shows total arsenic and copper concentrations. Comparing with the world average concentration of arsenic in river sediments (5 mg kg^{-1}) (19), it can be stated that all sampling locations except for Tinguiririca River (site 6, Figure 2) are impacted by arsenic pollution. Particularly high amounts of arsenic and also copper were found in sediments of the Coya River (site 1, Figure 2), which impacts the Cachapoal River (site 3, Figure 2) by mobilization of suspended particles as stated above. The situation of the Coya River is similar to that of other sediments contaminated with acid mine drainage detected in Europe and USA, in some cases containing over 2000 mg kg^{-1} arsenic (21). As in the case of the surface water under analysis, the lowest level of arsenic was found in the Tinguiririca River (site 6, Figure 1), which suggests that this

place could be used as a baseline in future monitoring studies in order to evaluate the impact of arsenic in the area.

The highest concentrations of total arsenic extracted with $1 \text{ mol L}^{-1} \text{ HCl}$ were found in sediments from the Coya River (27.2 mg kg^{-1}), corresponding to 21% of total arsenic. Speciation studies of the $1 \text{ mol L}^{-1} \text{ HCl}$ extract indicated that the predominant species was As(V) which is consistent with the fact that the most stable species associated with particulate matter is As(V) (22). It is well known that under reducing conditions As(V) is reduced to As(III), which is more weakly retained by iron and manganese oxides and can be released to water (23).

The arsenic extracted with $1 \text{ mol L}^{-1} \text{ HCl}$ could represent As associated with iron oxides and arsenic coprecipitated with acid-volatile sulfides in the sediment. The possible extraction mechanism corresponds to both proton dissolution and Fe-Cl complexation (24,25).

Table 3. Arsenic and copper concentrations (total and extracted with $1 \text{ mol L}^{-1} \text{ HCl}$) in sediment samples collected in November 2001.

Samples	Total As (mg kg^{-1})	Total Cu (mg kg^{-1})	As extracted with $1 \text{ mol L}^{-1} \text{ HCl}$, (mg kg^{-1})	Cu extracted with $1 \text{ mol L}^{-1} \text{ HCl}$, (mg kg^{-1})	Cu/As ratio
Coya River (1)	132	4.55×10^3	27.2	422	34.5
Cachapoal River (2)	18.2	759	6.60	21.2	41.7
Cachapoal River (3)	86.5	2.00×10^3	6.80	238	23.1
Alhué Stream (4)	36.0	502	NM	NM	13.9
Cachapoal River (5)	77.0	2.56×10^3	NM	NM	33.1
Tinguiririca River (6)	3.0	217	NM	NM	12.3

Numbers in brackets refer to sampling sites in Figure 2.
NM: not measured

Soil samples

Table 4 shows the concentrations of total arsenic in soil and the amount extracted with $1 \text{ mol L}^{-1} \text{ HCl}$. It is seen that in all the soil samples the amount of arsenic extracted with $1 \text{ mol L}^{-1} \text{ HCl}$ is low relative to total arsenic, which indicates that arsenic in these soils is present in a stable form. This low mobilizing capacity would decrease the probability of absorption by plants or release of arsenic to groundwater. HCl extraction has been used in soil to determine the probable As availability (10). However, Ng et al. (26) found that there was no significant correlation between As bioavailability and leaches using $1 \text{ mol L}^{-1} \text{ HCl}$. On the other hand, Shiwatana et al. (27) found that when a sequential extraction technique was used, HCl-soluble soil arsenic involved, besides As bound to Ca, As associated with Fe and, to a lesser extent, with Al.

High dispersion can be seen in the concentration found in soil of both total As and the As contained in the $1 \text{ mol L}^{-1} \text{ HCl}$ extract. High concentrations of arsenic were found in areas close to as well as farther away from the source of contamination (smelter). In the town of Coya, which is the place closest to the smelter, the highest concentrations were found at one of the points sampled.

Locations further away from the smelter, such as Machalí, Graneros and Rengo, also have high arsenic concentrations, which suggest that, in the case of Machalí, irrigation with water from the Cachapoal river could be responsible for the observed effect; in the case of Graneros and Rengo, the wind direction would favor the transport and soil deposition of airborne particles coming from the smelter.

Table 4. Arsenic concentrations (total and extracted with $1 \text{ mol L}^{-1} \text{ HCl}$) in soil samples collected in November, 2001.

Samples	Total As (mg kg^{-1})		As extracted with $1 \text{ mol L}^{-1} \text{ HCl}$ (mg kg^{-1})	
	0-10 cm	10-50 cm	0-10 cm	10-50 cm
El Álamo (S1)	34.2	14.0	5.40	3.50
Coya (S2)	62.2	42.2	3.60	1.80
Coya (S3)	205	181	7.90	8.50
Machalí (S4)	123	100	6.80	6.60
Graneros (S5)	333	316	7.50	7.90
Codao (S6)	100	85.2	0.200	0.500
Rengo (S7)	120	82.4	7.30	7.50
Pintué (S8)	25.9	9.20	1.50	0.900
Rangue (S9)	NM	NM	0.900	1.30

Numbers in brackets refer to sampling sites in Figure 2.
NM: not measured

Arsenic in Fish and Shellfish

Taking into account that the method based on hydride generation-cold trap-ICP has the restriction that it is only applicable to arsenic species which can be converted to arsines (inorganic and methylated arsenic species), arsenic speciation in fish (black kingclip, Chilean hake, and croaker) and shellfish (clam, mussel and barnacle) was carried out by HPLC-ICP-MS according to a previously reported procedure (14). The different fish and shellfish species were collected in the Pacific

Ocean, close to the Cachapoal River outflow.

As can be seen in Table 5, the amount of total arsenic found in these samples was lower than 26 mg kg⁻¹, and more than 72% is mainly present as arsenobetaine. A lot of information has been collected on the levels of arsenic in marine animals, showing considerable variability, although subsequent work revealed that arsenobetaine was the major arsenic compound in a large range of marine animals (28).

Table 5. Arsenic speciation in edible tissues of fish and shellfish.

Common Name	Scientific name	Total As* (mg kg ⁻¹)	As(V) (mg kg ⁻¹)	MMAA (mg kg ⁻¹)	DMAA (mg kg ⁻¹)	AB (mg kg ⁻¹)	AB (%)
Black kingclip	<i>Genypterus maculatus</i>	25.8	0.550	0.300	0.460	24.5	94.9
Chilean hake	<i>Merluccius gayi</i>	2.90	0.320	0.210	0.270	2.09	72.1
Croaker	<i>Cilus montti</i>	1.70	0.100	ND	ND	1.60	94.1
Clam	<i>Protothaca thaca</i>	8.50	ND	ND	ND	8.50	100
Mussel	<i>Mytilus chilensis</i>	23.0	0.880	ND	2.26	19.9	86.3
Barnacle	<i>Megabalanus psittacus</i>	9.90	0.260	ND	0.200	9.44	95.4

*Sum of arsenic species analyzed.

Concentration as dry weight

ND: not detected

CONCLUSION

The proposed method for arsenic speciation provides a good level of analytical features, which allows its application to environmental studies.

In both matrixes, water and sediment, arsenic was mainly present as As(V) and methylated arsenic species were not detected. The presence of high concentrations of arsenic and copper found in most of the matrixes under study suggests a real impact of the mining activity over the region. Arsenic in water and sediments has probably come from acid drainage, because pollution clearly diminished with increasing distance from the source. In the case of soil, it may 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 airborne particles deposited in soils. At the more impacted sites, arsenic is mostly immobilized as a form not available to plants.

Arsenic speciation in fish and shellfish collected in the Pacific Ocean at the Cachapoal River outflow shows that, probably, the contamination effect seen in river water has not yet reached the adjacent marine aquatic system.

The locality chosen for the study corresponds to a highly complex environmental system, where arsenic speciation has not been previously approached. Some assumptions made in this study serve to explain precise events occurring in the area. Nevertheless, it is difficult to make general assumptions that explain the contamination and mobilization of arsenic in the system, considering that there are precise emission sources (liquid wastes) and a series of diffuse sources (airborne particles mainly coming from the copper smelter), the effect of which is difficult to consider at each of the analyzed sites.

Incorporation of the data set obtained in this study into future environmental models that also consider meteorological and air quality data, would make it possible to determine more accurately the influence

of each of the emission sources, both precise and diffuse, in the region. In addition, producing an environmental model applicable to the area under study would allow the estimation of possible environmental episodes that might jeopardize the population around the smelting area as well as the organisms that live in it.

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