



PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
ESCUELA DE INGENIERIA

LOA RIVER GEOCHEMISTRY: ARSENIC DISTRIBUTION IN SEDIMENTS

ALEJANDRO DAVID FLORENZANO ALVO

Thesis submitted to the Office of Research and Graduate Studies in
partial fulfillment of the requirements for the Degree of Master of
Science in Engineering

Advisor:

PABLO PASTÉN

Santiago de Chile, January, 2009

© 2009, Alejandro Florenzano



PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
ESCUELA DE INGENIERIA

LOA RIVER GEOCHEMISTRY: ARSENIC DISTRIBUTION IN SEDIMENTS

ALEJANDRO DAVID FLORENZANO ALVO

Members of the Committee:

PABLO PASTÉN

GONZALO PIZARRO

CARLOS BONILLA

JOSÉ MANUEL DEL VALLE

Thesis submitted to the Office of Research and Graduate Studies in partial
fulfillment of the requirements for the Degree of Master of Science in
Engineering

Santiago de Chile, January, 2009

TABLE OF CONTENTS

	Page
INDEX OF TABLES	iv
INDEX OF FIGURES	v
ABSTRACT	vi
RESUMEN.....	vii
ACKNOWLEDGEMENTS	ix
1. INTRODUCTION	1
2. OBJECTIVES.....	4
3. LITERATURE REVIEW	5
3.1. Controls on arsenic mobility in freshwater sediments	5
3.1.1. Controls on arsenic mobility in oxidizing sediments	5
3.1.2. Controls on arsenic mobility in reducing sediments.....	7
3.2. Arsenic exposure in the Antofagasta Region	9
4. MATERIALS AND METHODS	10
4.1. Description of study area	10
4.2. Sampling sites	11
4.3. Water sampling and analysis.....	13
4.4. Sediment sampling.....	13
4.5. Total metal determination in sediments	14
4.6. Sequential extraction for As in sediments.....	15
4.7. X-ray diffraction.....	16
4.8. Statistical analysis	17
5. RESULTS AND DISCUSSION.....	18
5.1. Water analysis	18

5.2. Composition of sediment profiles	20
5.3. Elemental correlations in sediments.....	24
5.4. Selected study site: Loa at Sloman Reservoir	26
6. CONCLUSIONS	37
7. IMPLICATIONS AND FUTURE PERSPECTIVES.....	39
REFERENCES.....	41
APPENDIXES	48
APPENDIX A: Sampling apparatus.....	49
APPENDIX B: Sediment concentration profiles.....	50
APPENDIX C: Elemental correlations with arsenic in sediment cores by site.....	68
APPENDIX D: Sequential extraction procedure results	69
APPENDIX E: X-Ray Diffraction results	70

INDEX OF TABLES

	Page
Table 4-1. Sampling sites and geographic coordinates.....	12
Table 4-2. Sequential extraction procedure for As in sediments.	16
Table 5-1. Water parameters and dissolved element concentrations by site.....	18
Table 5-2. Mean, standard deviation, maximum and minimum values for selected chemical components.....	23
Table 5-3. Mineral phases identified by X-ray diffraction on three As-rich sediment samples.....	24
Table 5-4. Correlation coefficients of selected chemical components with As.....	25
Table 5-5. Correlation coefficients (R) for As with selected elements for a sediment core taken from the Sloman Reservoir in the Loa River.....	27
Table 5-6. Data used for modeling of aqueous and solid calcium arsenates.	32
Table 5-7. Saturation indexes for calcium arsenates and calcite obtained for Sloman Reservoir water data.....	32
Table 5-8. As speciation in waters of the Sloman Reservoir obtained by PHREEQC modeling.....	33

INDEX OF FIGURES

	Page
Figure 4-1. Schematic map of the Loa River Basin, sampling sites, and relevant features.	12
Figure 5-1. Dissolved arsenic vs. dissolved boron in water samples.....	20
Figure 5-2. Vertical distribution of As in sediments from the Loa Basin.....	21
Figure 5-3. Sediment cores taken from the Sloman Reservoir in the Loa River.	28
Figure 5-4. As, Fe, Ca, Mn and Sr content profiles for a sediment core taken from the Sloman Reservoir in the Loa River.....	28
Figure 5-5. Data clustering considering elemental compositions for samples from a sediment core taken from the Sloman Reservoir in the Loa River.	30
Figure 5-6. Arsenic extracted by each phase of the sequential extraction procedure for a sediment core taken from the Sloman Reservoir in the Loa River.	32
Figure 5-7. Arsenic to calcite ratio for sediment samples from the Sloman Reservoir..	35

ABSTRACT

Arsenic (As) in drinking water supplies is currently a worldwide issue of concern. This highly toxic element is consumed daily in dangerous concentrations by tens of millions of people, and yet the main processes controlling its speciation and mobility in natural environments are not fully understood, making it difficult to predict where dangerous concentrations will occur and what effects will anthropogenic or natural perturbations exert on its behavior. The Loa River Basin is known to be rich in As, affecting the inhabitants of the arid Antofagasta Region of Chile with severe health effects deriving from chronic exposure. Though some important processes controlling As concentrations in the zone have been previously established, such as hydrothermal input and high evaporation rates, the role of sediments in As cycling is far from clear. This study characterizes the distribution of As in shallow vertical sediment profiles at different sites in the basin. Lack of correlation between As and iron (Fe) within the cores suggest that Fe oxyhydroxides here are not effective at adsorbing As, likely due to a combination of elevated pH and competing ion concentrations in waters. Co-occurrence of As with calcium (Ca) at several sites suggests that calcite (CaCO_3) may play an important role in the input of As to the sediments. Evident stratification in sediments from the Sloman Reservoir suggests the deposition of As-rich calcite particles, exacerbated during major flood events. Sequential extraction of As from sediment samples from this site identified a high content of labile As, and therefore potential for liberation into the water column if disturbed. The identification and characterization of specific As-rich sediments poses an important contribution to focus further investigations. This system has unique conditions, such as its arid climate, alkaline waters and some of the highest concentrations of As reported in rivers in the world. It represents a model system for the study of As behavior, where there is an interaction between natural and anthropogenic sources, and where elevated concentrations may make it easier to observe processes that are also relevant elsewhere, in systems with lower As contents.

RESUMEN

El arsénico (As) en fuentes de agua potable es actualmente un tema de preocupación a nivel mundial. Este tóxico elemento es consumido diariamente en concentraciones peligrosas por decenas de millones de personas, y aún los principales procesos que controlan su especiación y movilidad no son bien comprendidos, haciendo difícil predecir dónde ocurrirán niveles peligrosos y qué efectos pueden ser causados por perturbaciones, ya sea naturales o antropogénicas, sobre su comportamiento. Es sabido que las aguas de la Cuenca del Río Loa son ricas en As, afectando a los habitantes de la árida Región de Antofagasta de Chile mediante severos problemas de salud derivados de la exposición crónica a este elemento. Aunque algunos procesos importantes que controlan las concentraciones de As en la zona han sido establecidos, tales como el aporte de fuentes hidrotermales y la importancia de la evaporación, el rol de los sedimentos en el comportamiento del As no ha sido elucidado. Este estudio caracteriza la distribución de As en perfiles verticales de sedimentos someros en distintos sitios de la cuenca. La ausencia de una correlación entre As y hierro (Fe) dentro de los perfiles sugiere que los oxihidróxidos de Fe en este sistema no son efectivos en adsorber As, probablemente debido a una combinación del alto pH con elevadas concentraciones de iones que compiten por sitios disponibles. La coocurrencia de As con calcio en varios sitios sugiere que la calcita (CaCO_3) puede jugar un rol importante en la incorporación de As a los sedimentos. La evidente estratificación observada en los sedimentos del Tranque Sloman sugiere la deposición de partículas de calcita ricas en As, exacerbada durante las grandes crecidas ocasionadas por el Invierno Boliviano. Los resultados de la extracción secuencial de As en sedimentos de este sitio muestran un alto contenido de As lábil y, en consecuencia, un potencial para su liberación a la columna de agua frente a perturbaciones. La identificación y caracterización de sedimentos específicos ricos en As contribuye de manera importante a enfocar futuras investigaciones. Este sistema tiene condiciones únicas, tales como su clima árido, aguas alcalinas y concentraciones de As entre las más altas reportadas para ríos en el mundo. Representa un sistema

modelo para el estudio del comportamiento del As, donde interactúan fuentes naturales y antropogénicas, y donde las elevadas concentraciones pueden facilitar el observar procesos que también son importantes en otros sitios con concentraciones más bajas.

ACKNOWLEDGEMENTS

This work was made possible by the funding from FONDECYT through the project 1070737/2007: *Evaluating competition of biotic and abiotic controls of As speciation in the solid phase in natural and engineered systems: integrating XAS, electron microscopy and mathematical modeling*, and from the U.S. National Science Foundation Grant EAR-0310657 (supplemented by the Hydrologic Sciences program and the Office of International Science and Engineering), through professors Aaron Packman and Jean-François Gaillard, from the Department of Civil and Environmental Engineering from Northwestern University, who collaborated in this research.

I would like to thank professors Pablo Pastén and Gonzalo Pizarro, and fellow researchers Marco Alsina, Alejandra Vega, Manuel Bugueño, Mathieu Hestin and Laura MacDonald for their important contributions in the field, the lab, and the development of this thesis.

I would also like to acknowledge the help from the Sociedad de Canalistas del Maipo, through the award of the Arturo Cousiño Lyon scholarship for Master of Science studies in the Hydraulic and Environmental Engineering areas.

1. INTRODUCTION

The effects of arsenic (As) on human health are currently a worldwide issue of concern. Chronic exposure to As has been associated to various diseases, such as arsenical dermatosis, hyperkeratosis, arsenicosis, cancer, and neurological disorders (Frankenberger, 2002; Pizarro et al., 2003; Cáceres et al., 2005).

Arsenic is the 20th most abundant element in the Earth's continental crust. It is widely distributed in the environment: it is found in surface and ground waters, soils, rocks, and living organisms (Smedley & Kinniburgh, 2002; Van Herreweghe et al., 2003). Although there are several possible human exposure paths to As, the greatest hazards today are caused by toxic concentrations of this metalloid in drinking water supplies.

Examples of public health issues related to the ingestion of As-rich water are found throughout the world, including West Bengal (India), Bangladesh, Vietnam, the USA, Mexico, Taiwan, Argentina, and Chile (Smith et al., 1992; Welch et al., 2000; Smedley & Kinniburgh, 2002). This list is rapidly growing, as the assessment of As levels in drinking waters and health effects on populations becomes widespread. Additionally, growing stress on water resources, especially aquifers, is causing the increasing release of As to drinking supplies. In the Bay of Bengal and Southeast Asia this problem has reached massive proportions, with tens of millions of people being exposed daily to dangerous As levels (Harvey et al., 2002; Postma et al., 2007). Both anthropogenic (e.g., infiltration of As-rich mine tailings, use of As-bearing pesticides) and natural (e.g., geothermal spring inputs, dissolution of As-rich minerals) sources are responsible for the presence of As in waters.

Given this widespread health risk, research on As behavior has become a very active area in the environmental sciences. It is of critical importance to gain knowledge on the processes that control its mobility and speciation in natural systems and water supplies.

These have proven to be a complex interaction of chemical (e.g., precipitation/dissolution, redox reactions, surface complexation), physical (e.g., convective and diffusive transport) and biological (e.g., microbial transformations) factors. Despite the abundant investigations worldwide and the important achievements that have been made in the area, a clear understanding of these processes has not yet been accomplished (Postma et al., 2007). The high variability of As-rich site characteristics (e.g., geology, hydrology, chemical conditions) makes it very challenging to produce models which are widely applicable. A better understanding of these interactions will allow for the design of appropriate abatement technologies, prediction of convenient water supply sources, and estimation of the effects of human activities on As distribution and its associated risks.

The Loa River Basin has unique conditions, such as its arid climate, alkaline waters and some of the highest concentrations of As reported in rivers in the world (Smedley & Kinniburgh, 2002). It represents a model system for the study of As behavior, where there is an interaction between natural and anthropogenic sources, and where elevated concentrations may make it possible to observe processes that are also relevant elsewhere, in systems with lower As contents.

This work studies the As content in vertical sediment profiles from the Loa River and its main tributaries in order to gain knowledge on possible processes that could control As mobility between the sediments and the water column. It aims to determine sites with elevated As concentrations, to identify possible remobilization hazards, immobilization mechanisms and suggest directions for further research.

The World Health Organization recommends a maximum permissible concentration of 10 µg/l for As in drinking water (WHO, 2006), posing a major challenge on scientists and engineers to propose technologies to reach and detect this low concentrations. This

work is aligned in that effort, trying to contribute to the understanding of As behavior in the Loa River Basin and, more generally, in the environment.

2. OBJECTIVES

- Contribute to the geochemical characterization of Loa River Basin system, with an emphasis on As. More information on the composition of water and sediments will help to evaluate the potential impact of future human activities, such as increasing water abstractions for human consumption, and industrial and mining activities.
- Determine the As content in vertical sediment profiles from the Loa River and its main tributaries, and identify correlations with other elemental concentrations and water quality parameters, to gain knowledge on possible processes that could control As mobility between the sediments and the water column.
- Determine locations with elevated As concentrations to identify possible remobilization hazards, immobilization mechanisms, interesting sites for the application of more specific analytical techniques, and the study of abiotic and biotic controls on As (e.g., plant or microbial interactions).

3. LITERATURE REVIEW

3.1. Controls on arsenic mobility in freshwater sediments

Arsenic (As) is found in freshwaters mainly as the inorganic oxyanions arsenate [As(V)] and arsenite [As(III)], thermodynamically favored under oxic and reducing conditions, respectively. Nevertheless, they usually coexist in both types of environments due to microbial transformations (Nicholas et al., 2003; Oremland & Stolz, 2003). Methylated As species are also commonly present, but at minor concentrations, except for waters with elevated primary productivity where they could be significant (Francesconi & Kuehnelt, 2002).

Sediments play an important role in the cycling of As in lacustrine and fluvial environments. They may act as a sink, accumulating As-bearing particles settled from the overlying waters. After this deposition, though, As is not static in the sediment column. Various factors control its associations, speciation, mobility, and potential liberation to the water column.

Redox conditions within the sediment column have been identified as being one of the main factors controlling As environmental behavior (Moore et al., 1988; Kneebone et al., 2002). There are distinct processes occurring in oxidizing and reducing environments, and an interaction thereof caused by vertical redox gradients commonly found within sediments.

3.1.1. Controls on arsenic mobility in oxidizing sediments

Arsenic oxyanions have a strong tendency to adsorb to metal oxide surfaces, particularly to hydrous Fe oxides, which have been shown to be the main mechanism of As removal from solution in oxic environments (Moore et al., 1988; O'day et al., 2004). Mn and Al

oxides and phyllosilicates are also likely to play a role in providing surfaces for As sorption (Smedley & Kinniburgh, 2002; O'day et al., 2004).

As(V) and As(III) have different affinities for sorbent phases. These affinities are highly dependent on pH. As(V) adsorption to iron oxide minerals has been shown to be favored at acidic and circumneutral pH, while As(III) is most strongly sorbed at higher pH values (Dixit & Hering, 2003). As(V) reduction (unaccompanied by host oxide mineral reduction) will thus cause desorption from oxides under many environmental conditions. Nevertheless, in alkaline environments it can even enhance sorption. An increase in pH, as could be caused by mineral weathering combined with high evaporation rates in arid areas (Smedley & Kinniburgh, 2002), would probably cause As(V) desorption from oxides and increased levels of dissolved As.

Reductive dissolution of host phases will release significant amounts of sorbed As to porewater (Kneebone et al., 2002; Martin & Pedersen, 2002; Keimowitz et al., 2005). The limitation on oxygen diffusion due to low sediment permeability or oxygen depletion in overlying waters, coupled with organic matter deposition, will generate reducing conditions, under which an important fraction of As-bearing oxides will dissolve and release As to porewaters (mostly in the more toxic form As(III)), part of which may diffuse onto the overlying water body. This phenomenon is observed seasonally in eutrophic lakes that are subject to summer anoxia (Jay et al., 2005).

In-situ removal of As from water supplies by coagulation-flocculation processes can be an important input to sediments, where avoiding remobilization is of critical importance. An example of this is found in the Los Angeles Aqueduct, water source for the city of Los Angeles, California (Kneebone et al., 2002), where ferric chloride and a cationic polymer are added to the water supply to form iron oxyhydroxide floc which sorb the As and settle at a reservoir. As has been shown to be released to porewater at depth, tightly coupled to Fe dissolution, and is maintained trapped in the sediments only because of the

continuous deposition of Fe oxides which serves as a sorptive barrier for the migration to the overlying reservoir. If this treatment were to be stopped, it is likely that the lack of a Fe-rich superficial sediment layer would bring upon the massive release of As onto the drinking water supply, causing a major health emergency.

Competition for available sorbent surfaces with other solutes, such as phosphate, and to a lesser extent bicarbonate, silicate, sulfate, and organic matter, has been shown to be an important factor affecting As mobility in sediments (Wilkie & Hering, 1996; Reynolds et al., 1999; McNeill et al., 2002; Smedley & Kinniburgh, 2002).

Precipitation of As in mineral phases under oxic conditions is unlikely to be quantitatively significant in natural waters, since most arsenate minerals are highly soluble under regular environmental conditions (Hering & Kneebone, 2002).

3.1.2. Controls on arsenic mobility in reducing sediments

Under reducing conditions, where Fe oxides are unstable, the main control on As mobility is the presence of sulfides, through sorption onto sulfide minerals, precipitation of As sulfides and coprecipitation with Fe sulfides (Moore et al., 1988; Bostick & Fendorf, 2003; O'day et al., 2004).

Both As(III) and As(V) have been shown to sorb onto Fe sulfide mineral surfaces both in laboratory (Bostick & Fendorf, 2003; Wolthers et al., 2005) and environmental conditions (Bostick et al., 2004). As(III) has been shown by X-ray Absorption Spectroscopy (XAS) analysis to form FeAsS-like surface precipitates on FeS, which under persisting sulfidic conditions tend to convert to the more stable mineral orpiment (As_2S_3) (Bostick & Fendorf, 2003). There is also evidence for the formation of realgar (AsS) in high Fe sediments. Coprecipitation with FeS and pyrite (FeS_2) is well

documented as an important sink for dissolved As, as well as other trace elements, from solution (Huerta-Díaz et al., 1998).

Elevated sulfide concentrations will not necessarily result in a decrease in dissolved As concentrations. Under certain conditions, the formation of thioarsenites (aqueous As(III)-sulfide complexes) may increase As solubility and thus cause elevated As concentrations in porewaters. The formation of these complexes is highly dependent on pH and sulfide concentration. The presence of reactive iron will inhibit the formation of these species, as Fe scavenges S from solution (Inskeep et al., 2002; Wilkin et al., 2003). The behavior of these compounds and their environmental relevance is yet poorly understood, since few studies have considered them and they are often mistaken for arsenite through conventional analytical techniques.

The Fe/S ratio has been shown to play an important role on As mobility in sulfidic environments. A geochemical reaction path model for the Fe-S-As system under reducing conditions, based on spectroscopic observations of solid phases at a contaminated site and published solubility data, establishes two characteristic reaction paths for As under increasingly sulfidic conditions (O'day et al., 2004). According to this model, under high reactive Fe/S ratios, where dissolved sulfide concentrations are buffered by the formation of Fe-sulfides such as pyrite (FeS_2), As(III) will precipitate as realgar (AsS). Under low reactive Fe/S ratios, without sulfide buffering, orpiment (As_2S_3) is formed, and with increasing sulfide concentrations, it is dissolved onto the aqueous $\text{AsS}(\text{OH})(\text{SH})^-$.

Even though Fe oxide minerals are thermodynamically unfavored under reducing conditions, they are subject to slow dissolution kinetics, and thus persist in sediments where their presence would not be predicted by equilibrium calculations, providing a surface for sorption. As(III) has been shown by XAS analysis to remain associated to Fe

oxyhydroxide phases under reducing conditions in buried sediments (Kneebone et al., 2002).

In the absence of sulfide, oxide mineral dissolution will cause As, mainly as As(III), to accumulate in porewaters, without any important mechanisms to bind it to the solid phase, accompanied by Fe and Mn which will be in their more soluble (+2) oxidation states (Keimowitz et al., 2005). This situation is usually found in redox transition zones, where oxides are unstable and the redox potential is not low enough for sulfate reducing conditions.

3.2. Arsenic exposure in the Antofagasta Region

The fact that the waters of the Loa River Basin have elevated As concentrations is well known. The population of the area has been exposed to toxic levels of this pollutant, particularly before the installment of water treatment plants for the main urban centers, Calama and Antofagasta, in 1969 (Smith et al., 1998). This exposure has been related to elevated fetal and infant mortality (Hopenhayn-Rich et al., 2000), lung and bladder cancers, vascular diseases, and skin lesions (Ferreccio & Sancha, 2006).

Even though water treatment for cities has reduced health hazards, it has not eliminated them. The Chilean standard for As in drinking water establishes a maximum concentration of $50 \mu\text{gL}^{-1}$ (five times higher than the WHO recommendation), which has been found to be unsafe for human consumption (Ferreccio & Sancha, 2006). Some rural communities still depend on untreated As-rich waters as their drinking source, with consequential effects including skin lesions and keratosis, such as the ones detected in the people of the Chiu Chiu village, enduring As intakes of up to $800 \mu\text{g/l}$ (Smith et al., 2000). Additionally, dangerous As concentrations have been found in river-dwelling fish and river-irrigated crops in the region (Queirolo et al., 2000b; Pizarro et al., 2003), which represent alternative routes for human intake.

4. MATERIALS AND METHODS

4.1. Description of study area

The Antofagasta Region is located in the Atacama Desert in the north of Chile. The main permanent surface water bodies in this extremely arid region are the Loa River and its tributaries. Together with groundwater resources, they are used to serve drinking and irrigation demands for its population of approximately half a million, and from the intense mining activity that takes place in the area, mainly copper extraction and smelting.

The Loa River is born in an active volcanic area of the Andes mountain range, at an altitude over 4000 m above sea level. It travels for approximately 440 km before it reaches the Pacific Ocean, receiving waters from several tributaries on the way (San Pedro, Salado, and San Salvador rivers are the main ones).

Romero et al. (2003) studied the As enrichment in the Loa River Basin (main features shown in Figure 4-1), thoroughly analyzing water and sediment samples to characterize its distribution and to identify possible sources and controlling processes. They concluded that the main As source in the area is natural, related to the zone's lithologies.

The main As input is believed to be the El Tatio Geyser field, with As concentrations up to 27 mg/l (some of the highest reported in natural waters in the world), which feeds the Salado River (As concentrations ranging from 1 to 10 mg/l). The Salado then joins the Loa, which carries lower As contents before the junction (0.3 mg/l). From that point to the outlet to the Pacific Ocean, As concentrations gradually go from approximately 1 mg/l up to 2 mg/l, presumably due to high evaporation rates in this arid zone (Romero et al., 2003). Additional sources of As to the system are solid waste, airborne emissions, and tailings from past and present mining activity. The nature and extent of this

influence is yet to be assessed. Detailed descriptions of the geologic, hydrologic, and demographic features of the region are given elsewhere (May et al., 1999; Queirolo et al., 2000a; Romero et al., 2003)

Concentrations found in sediments by Romero et al. (2003) varied within the Loa Basin, ranging from 26 to 2000 mg/kg, with an average of 320 mg/kg, which exceeds by at least 30 times the average concentrations described for fluvial sediments, and are only comparable to those reported for highly contaminated industrial sites (Smedley & Kinniburgh, 2002). These elevated concentrations suggest that sediments may play an important role in the As cycling in the system. Furthermore, they represent a massive reservoir of this highly toxic element, and it is of great importance to understand the interactions occurring both in the sediment/water interface and within the sediments in order to assess under what conditions this As could be mobilized.

Previous studies analyzed river sediments, but did not take into account the vertical variability within the sediments. This variability may be caused by sediment deposition history and by processes occurring within the sediments, such as changing redox conditions, sorption/desorption, or mineralization.

4.2. Sampling sites

On June 2007 a sampling campaign was performed. Water samples were taken at 21 different points of the Loa River and its main tributaries, the Salado and San Salvador rivers. At 14 of these point sediment cores were also taken. Figure 4-1 shows the sampling points, and Table 4-1 shows its names and coordinates.

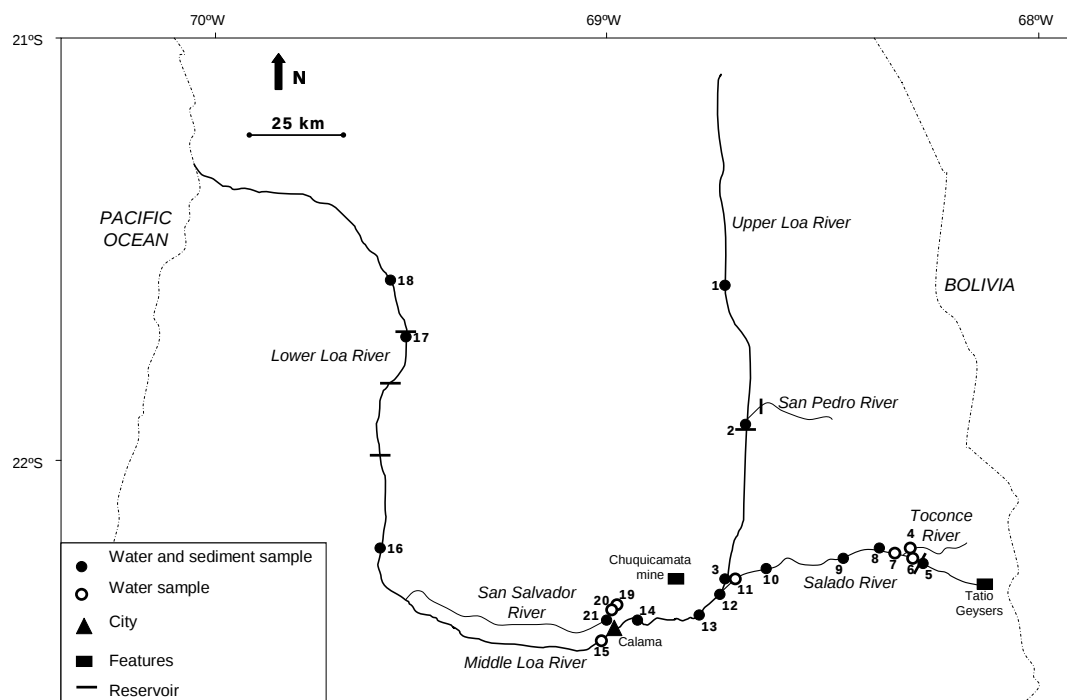


Figure 4-1. Schematic map of the Loa River Basin, sampling sites, and relevant features.

Table 4-1. Sampling sites and geographic coordinates (continued on the next page).

Zone	Nº	Site Name	Longitude	Latitude	Altitude (m.a.s.l.)
Upper	1	Loa Lequena	21°39'00"S	68°39'47"W	3315
Loa	2	Loa Conchi Reservoir	22°00'10"S	68°36'39"W	2996
	3	Loa before Salado	22°22'12"S	68°39'18"W	2511
Toconce	4	Toconce before Salado	22°16'43"S	68°12'44"W	3099
Salado	5	Salado Codelco Reservoir	22°17'11"S	68°12'00"W	3173
	6	Salado before Toconce	22°16'49"S	68°12'41"W	3095
	7	Salado after Toconce	22°16'39"S	68°13'53"W	3061
	8	Salado Spring	22°16'39"S	68°13'54"W	3063
	9	Salado Ayquina	22°17'14"S	68°20'28"W	2954
	10	Salado Baden	22°19'58"S	68°33'27"W	2557
	11	Salado before Loa	22°22'15"S	68°39'16"W	2508

Middle	12	Loa after Salado	22°22'16"S	68°39'20"W	2501
Loa	13	Loa Angostura	22°27'28"S	68°43'49"W	2464
	14	Loa Yalquincha	22°27'02"S	68°52'46"W	2312
	15	Loa Finca	22°30'29"S	69°00'01"W	2063
Lower	16	Loa Cruce	22°13'36"S	69°33'40"W	1139
Loa	17	Loa Sloman Reservoir	21°51'14"S	69°30'52"W	920
	18	Loa Quillagua	21°40'47"S	69°31'40"W	806
San	19	San Salvador Spring – Brine	22°26'28"S	68°57'25"W	2215
Salvador	20	San Salvador Spring - Running Water	22°26'28"S	68°57'25"W	2215
	21	San Salvador Wetland	22°26'40"S	68°58'26"W	2194

4.3. Water sampling and analysis

Water quality was assessed as follows:

- Water pH, temperature and conductivity were measured in-situ.
- Cl^- was determined using an ion selective electrode in the laboratory on a filtered sample (0.45 μm mixed cellulose ester membranes, Millipore).
- Water samples for total metal determination were acidified to $\text{pH} < 2$ with Suprapure HNO_3 (Merck).
- Samples for dissolved metal determination were filtered and acidified.
- All samples were stored in polypropylene bottles at a temperature under 5°C until analysis.
- Metals were determined by ICP-AES (Thermo, iCAP 6300). Samples for total metal determination were digested with aqua regia on a hot plate before ICP-AES analysis.

4.4. Sediment sampling

Cores were taken from locations which showed sediment accumulation and which were morphologically representative of the sampled areas. At three sampling stations, where

heterogeneous material accumulation characteristics were observed (Salado Ayquina, Salado Codelco Reservoir, and Loa Cruce), two sediment cores were taken (labelled A and B) from different sectors.

Sediment sampling was done using a hand-piston corer with interchangeable acrylic tubes with a 5 cm diameter. At most sites it was possible to wade into the middle of the river section to take the core, being careful not to disturb the zone to be sampled. Exceptions were made in the sampled reservoirs (Conchi, Codelco, and Sloman), where cores were taken near the border.

Seventeen cores were extracted, ranging from 5 to 26 cm in depth, depending on the ability to insert the corer at each site. The cores were sectioned on-site onto 1, 2 or 3 cm intervals with a plastic knife, and stored separately for transport to the lab on iced coolers, and maintained under 5°C until analysis.

4.5. Total metal determination in sediments

Metal determination in sediment samples was done using an aqua regia extraction procedure adapted from the standard ISO/CD 11466 (ISO, 1995). Aqua regia has been shown to be an appropriate extractant for As and metals from soils and sediments (Tighe et al., 2004; Loska & Wiechula, 2006). Nevertheless, it is considered a “pseudototal digestion” (García-Manyes et al., 2002), for it will not dissolve As bound to silicates, which are likely to be present in sediments from the Loa Basin (Romero et al., 2003).

Sediment samples were dried (4 hours at 105°C) and ground onto a homogenous fine powder using agate mortar and pestle. A 0.5 g aliquot of each dry sediment sample was placed into a borosilicate beaker, and 12 ml aqua regia (3:1 HCl/HNO₃) was added. The beakers were covered with watch glasses and left for 16 hours at room temperature. Later, they were heated for 2 hours on a hot plate at approximately 80°C. After the first

hour of heating the watch glasses were removed, and small amounts of 1% v/v HNO₃ were periodically added to avoid drying of the samples. The samples were allowed to cool and then were filtered on Whatman 41 filter papers. The samples were taken to 50 ml with 1% v/v HNO₃, thoroughly washing beakers and filters. All reagents used were of analytical grade or better (Merck), and Milli-Q water was used for the whole process.

These samples were analyzed by ICP-AES (Thermo, iCAP 6300) for a suite of elements. Detection limits for this method are estimated to be 3 mg/kg for Fe and 1 mg/kg for the other measured elements. Most samples showed detectable concentrations of As, Sb, Cu, Fe, Mn, Ni, Pb, Zn, Ca, K, Mg, Na, Al, B, Ba, Co, Cr, V and Sr, but were under the detection limit for Ag, Bi, Se, and Tl.

Nine samples from different cores were analyzed in duplicate, to test for method reproducibility. All samples showed a difference under 16% for As (mean=9%, SD=6%). Other elemental concentration discrepancies were under 20% for most samples. Three digested samples were spiked with known As concentrations to evaluate possible matrix interferences on ICP-AES measurements. Discrepancies with expected results were under 10% for all cases (mean=4%, SD=5%). Multi-element standards (Merck) were measured with each batch of samples to test for equipment accuracy, and always showed under 10% difference with expected concentrations.

4.6. Sequential extraction for As in sediments

A second sampling campaign was done in July 2008, specifically to retrieve sediment cores for a sequential extraction procedure designed to target As phases commonly found in sediments (Keon et al., 2001). These cores were immediately capped after retrieval and frozen on dry ice, as to minimize porewater flux and potential artifacts caused by storing and handling conditions (Rapin et al., 1986; Peltier et al., 2005). They were unfrozen and handled inside an anaerobic chamber filled with N₂, in order to

prevent the oxidation of reduced species (such as As or Fe sulfides) which could be present. Here they were sectioned every 2.5 cm, and a 0.4 g aliquot of wet sediment was taken for the sequential extraction.

These aliquots were ground onto fine powder and put into 50 ml gas-tight centrifuge tubes, where the extractants were added. They were shaken on an orbital shaker for the duration specified by the protocol, centrifuged for 30 minutes at 6000 RPM and reinserted onto the anaerobic chamber for the removal of the supernatant using syringes with plastic tips. The supernatants were taken to 1% v/v HNO₃ and analyzed by ICP-AES. The first three steps of the protocol proposed by (Keon et al., 2001) were applied to each sample. These steps are summarized in Table 4-2.

Table 4-2. Sequential extraction procedure for As in sediments. (Adapted from Keon et al., 2001).

Step	Extractant	Target phase
1	1 M MgCl ₂ (pH=8)	Ionically bound As
2	1 M NaH ₂ PO ₄ (pH=5)	Strongly adsorbed As
3	1 N HCl	As coprecipitated with acid volatile sulfides, Mn oxides, carbonates and very amorphous Fe oxyhydroxides

4.7. X-ray diffraction

Mineral identification by X-ray diffraction (XRD) for selected samples was done with a Rigaku diffractometer. Patterns were collected over 20-70° 2θ angles with the system operating at 40 kV and 20 mA (nickel filtered Cu K-α radiation, 0.05° 2θ steps, 1 sec/step). Diffraction peaks were identified using Jade 5.0 (Materials Data, Inc.) processing software.

4.8. Statistical analysis

Hierarchical clustering of sediment composition data was done using the StatistiXL software (Roberts & Withers, 2007)). Distance/similarity was measured by the Bray and Curtis method, while data clustering was done by the Nearest Neighbor method. Element to element correlation analysis for each sediment core was also done using this software.

5. RESULTS AND DISCUSSION

5.1. Water analysis

The main results from the water analysis are shown in Table 5-1. These data resemble previous findings, with As concentrations relatively low in the Upper Loa (still more than four times the national standard and 20 times the standard suggested by WHO), extremely high in the Salado, and increasing from the Medium Loa to the Upper Loa and to the outlet.

Table 5-1. Water parameters and dissolved element concentrations by site. Dash indicates parameter not measured.

Zone	Site N°	pH	T (°C)	Condu- ctivity (ms/cm)	Dissolved concentration in water (mg/l)														
					As	Fe	Mn	Mo	Sb	Al	B	Li	Sr	Zn	Ca	K	Mg	Na	Cl-
Upper Loa	1	-	17.4	1.2	0.22	0.16	0.02	<0.01	<0.01	0.17	4.01	<0.01	0.21	0.02	84	16	28	126	195
	2	-	12.9	3.2	0.20	0.03	0.02	0.01	<0.01	0.14	6.91	0.18	1.26	0.03	195	32	111	395	775
	3	8.3	12.9	3.4	0.24	0.05	0.02	0.01	<0.01	0.19	9.20	<0.01	1.74	0.05	160	35	115	435	894
Toconce	4	8.5	8.7	2.8	1.30	0.03	0.01	0.01	0.01	0.13	8.70	0.07	1.02	0.01	94	33	30	412	894
Salado	5	8.4	15.1	8.0	10.82	0.03	0.10	0.02	0.48	0.03	49.08	2.59	1.10	0.03	125	120	15	1406	2881
	6	8.4	6.8	8.9	12.54	0.04	0.10	0.02	0.58	0.15	55.64	3.34	1.32	0.03	156	141	18	1682	3297
	7	7.9	7.6	6.6	7.64	0.26	0.12	0.02	0.32	0.08	36.97	1.86	1.29	0.03	134	94	25	1143	2435
	8	6.3	23.2	9.7	0.28	<0.03	6.72	<0.01	<0.01	<0.01	11.41	0.77	11.13	0.10	410	128	131	1683	2751
	9	7.2	10.6	7.1	4.06	0.14	0.54	0.01	0.18	0.07	25.89	1.77	4.62	0.19	233	93	59	1259	2334
	10	8.3	8.9	14.1	1.17	0.01	<0.01	0.01	0.05	0.06	14.98	0.52	7.22	0.01	198	100	98	1271	2276
	11	8.1	10.4	7.3	1.24	0.11	0.02	0.01	0.04	0.17	16.73	1.14	7.46	0.03	196	101	99	1306	2414
Middle Loa	12	8.1	10.7	6.0	0.92	0.04	0.02	0.01	0.02	0.16	13.86	1.34	5.29	0.01	186	79	106	1022	1997
	13	7.6	13.1	6.5	1.06	0.06	0.03	0.01	0.02	0.04	12.62	<0.01	4.69	0.06	219	69	103	974	2057
	14	8.2	15.0	6.9	1.01	0.03	0.02	0.01	0.01	0.18	12.36	0.63	4.46	0.03	234	70	111	1043	2191
	15	8.2	14.9	7.6	1.40	0.04	0.02	0.01	0.03	0.18	12.11	0.31	3.52	0.02	255	83	141	1313	2210
Lower Loa	16	8.3	12.3	10.2	1.70	0.08	0.02	0.02	0.02	0.12	20.38	<0.01	5.32	0.06	346	116	200	1768	3424
	17	8.7	15.1	13.9	1.91	0.04	0.02	0.02	0.01	0.21	29.04	1.21	7.95	0.02	426	151	268	2413	4316
	18	8.2	15.0	15.2	1.70	0.11	0.03	0.03	0.02	0.13	32.27	2.25	8.63	0.05	505	177	315	2659	5260
San Salvador	19	8.5	-	-	3.55	0.04	0.04	3.60	0.02	-	-	-	-	0.03	-	-	-	-	-
	20	7.5	-	-	1.09	0.04	0.01	0.36	<0.01	0.16	28.25	<0.01	7.73	0.03	369	125	202	1600	-
	21	8.2	9.7	9.6	0.95	<0.03	0.01	0.27	0.01	0.11	25.41	2.44	6.87	0.01	332	117	193	1549	2315

Salado Spring site was a warm spring emerging a few meters away from the Salado River. It was thought to come from a geothermal source related to the Tatio Geysers, nevertheless, its composition contradicted this prediction, showing comparatively low As and B concentrations, and an extremely high Mn content. It is interesting also to mention that the Toconce River, which supplies water for the village with the same name, has an As concentration of over 1 mg/l.

Ag, Be, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl and V were under method detection limit for Total concentrations of As and Fe were not significantly different from dissolved concentrations (data not shown), with the exception of the brine sampled at San Salvador Spring, with total Fe 35 times higher than dissolved Fe, and total As 3 times higher than dissolved As. This site also shows elevated Cu and Mo total concentrations. Being a spring closely downhill from the Chuquicamata mine, in an area with a history of mining waste disposal, this evidence suggests that the elevated concentrations are influenced by this activity, representing an anthropogenic input of pollutants to the San Salvador and Loa rivers.

Arsenic versus boron (used as a conservative tracer) was plotted for three divisions of the basin. Upper Loa shows no significant correlation ($R^2 = 0.31$), Medium-Lower Loa shows a moderate correlation ($R^2 = 0.68$), while Salado shows an almost perfect linear correlation ($R^2 = 1.00$). This indicates that As would behave conservatively in the Salado River during normal flow conditions, controlled by evaporation and dilution, while in the Loa River either other processes are relevant, such as interaction with sediments or contribution from waters with different characteristics.

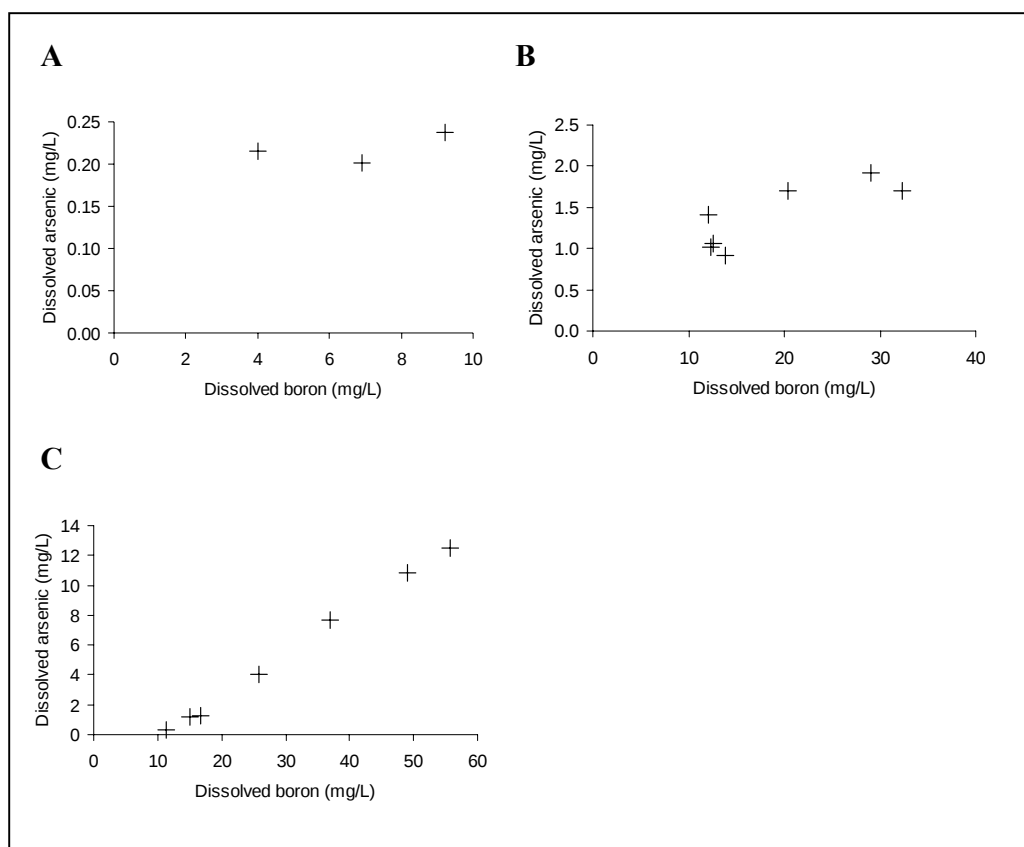


Figure 5-1. Dissolved arsenic vs. dissolved boron in water samples from **A:** Upper Loa River, **B:** Medium and Lower Loa River, and **C:** Salado River.

5.2. Composition of sediment profiles

Concentration profiles for As and 18 other elements were obtained for the 17 analyzed sediment cores. As profiles for the different cores and their location in the basin are shown in

Figure 5-2. Profiles for the other elements are not shown (summary in table Table 5-2). These results show that all along the basin the content of As in sediments is considerably high in comparison with those described for freshwater environment sediments elsewhere, mostly under 10 mg/kg. The highest average As contents are found in the San Salvador Wetland (604 mg/kg), the Salado River (414 mg/kg) and the Lower Loa (342 mg/kg).

Romero et al. (2003) found As concentration in the waters of the Loa Basin to be correlated to the As content of sediments at 5 cm depth ($R^2=0.70$). Our results show no clear correlation between dissolved As concentration in the water column and surface layer sediment As content ($R^2=0.006$) or between water As concentration and 5 cm depth sediment As content ($R^2=0.002$). Nevertheless, if samples from the reservoirs (Codelco, Sloman, and Conchi) and from San Salvador wetland are excluded, a positive correlation is found between water As concentration and 5 cm depth sediment As content ($R^2=0.60$).

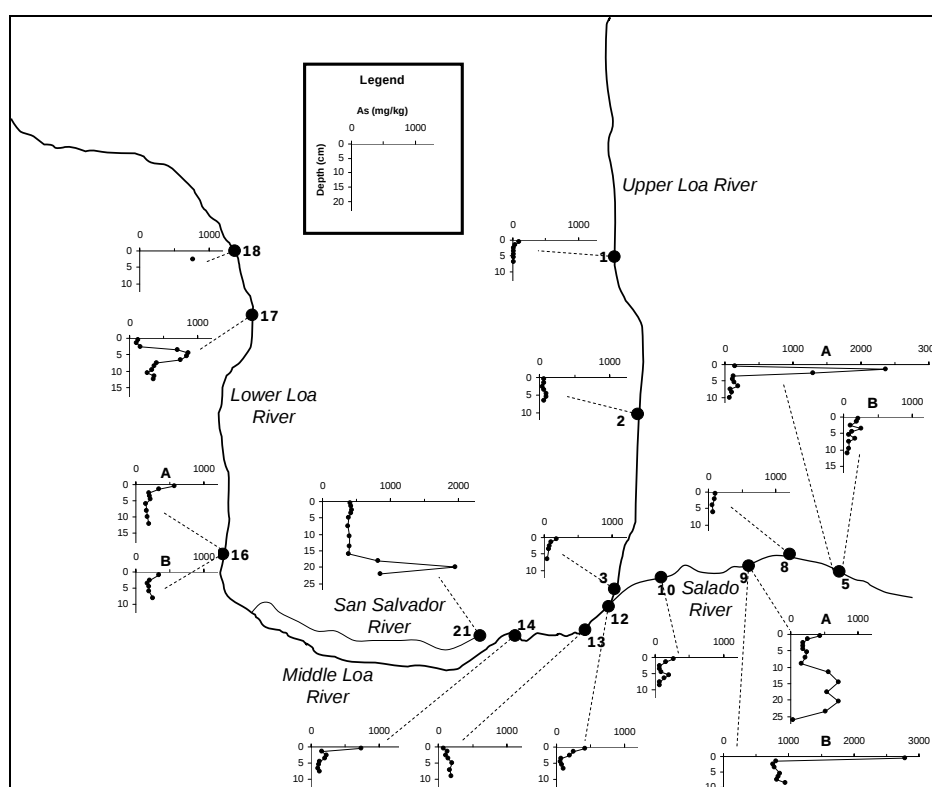


Figure 5-2. Vertical distribution of As in sediments from the Loa Basin. Horizontal axes indicate As content in sediments (mg/kg), and vertical axes indicate sediment depth (cm). Each data point is plotted at its middle depth. Sites where two cores were taken are labeled A and B.

The profile observed at San Salvador Wetland is of particular interest. This wetland is at the head of the San Salvador River, and it is formed by a series of groundwater springs. Abundant As is found in the deepest sampled sediments (17 to 23 cm), where apparently there is a high content of organic matter. This could be related to mining activity uphill (Chuquicamata), as the enrichment in the same stratum of Cu and other metals suggest. Sulfide phases could be present and responsible for metal immobilization, suggested by the dark appearance and characteristic sulfidic odor of this stratum. Further sediment characterization would be required to confirm this hypothesis.

A summary of the composition of the analyzed sediment cores is shown in Table 5-2, together with a comparison with data from a previous study (Romero et al., 2003). Our samples were taken from different depths ranging from 0 to 26 cm, while the previous study took samples from 5 cm depth. Even though our sampling focuses more on the vertical and less on the horizontal variability with respect to previous data, mean values for each of the river sectors are usually within the same order of magnitude for the 14 compared elements. Coherence between both data sets allows us to conclude that the values listed are actually representative of the mentioned sectors of the basin, with differences arising by the selection of sampling sites and the heterogeneity which is inherent to the system.

Major differences in reported sediment composition between both studies are found for San Salvador River. This is due to the fact that our samples were taken from the highly contaminated wetland at the head of the river, while the previous study's samples were taken from different parts along the course of the river.

Our results show that Ca, Fe and Al are the main measured components in the aqua regia extractable fraction in the analyzed samples. Salado River sediments are dominated by

Table 5-2. Mean, standard deviation, maximum and minimum values for selected chemical components (mg/kg) in sediments and comparison of the data from this work with data from a previous publication (Romero et al., 2003). n= number of samples. *: inconsistent data.

			Concentration in sediments (mg/kg)														
Zone		n		As	Ca	Fe	Al	K	Na	Mn	Sr	Cu	Ba	Ni	Zn	Co	V
Salado	This work	53	Mean	414	15043	35081	15745	3965	1905	448	147	46	177	8	106	16	158
			SD	541	19282	18024	4660	976	734	176	186	27	32	4	62	7	110
			Max	2789	98534	114534	27729	6032	4165	1041	1026	135	290	20	327	41	587
			Min	39	4674	20609	10249	617	651	220	30	15	131	4	43	8	71
	Romero et al.	14	Mean	250	19400	39500	21700	5100	2800	950	190	150	170	14	110	12	100
	Difference		Mean	66%	-22%	-11%	-27%	-22%	-32%	-53%	-23%	-69%	4%	-42%	-4%	34%	58%
Upper Loa	This work	20	Mean	62	121042	12598	8244	2298	1621	374	493	68	100	5	38	4	42
			SD	41	111865	2988	1672	2177	894	265	435	47	17	1	6	2	11
			Max	178	274333	19083	12404	10821	4615	978	1076	144	134	7	58	7	63
			Min	7	2868	8813	5972	691	475	93	27	15	63	4	27	0	26
	Romero et al.	10	Mean	120	48000	33000	27000	4800	2200	13*	330	270	170	13	90	9	90
	Difference		Mean	-48%	152%	-62%	-69%	-52%	-26%	2773%	49%	-75%	-41%	-60%	-58%	-58%	-53%
Medium Loa	This work	22	Mean	182	50024	18339	10914	3102	2511	563	327	71	115	8	101	8	68
			SD	149	14266	3660	3841	1129	1311	427	156	78	17	2	52	1	9
			Max	741	78500	25720	25190	5983	5941	1892	616	272	141	11	258	10	84
			Min	55	23329	13528	6797	1157	1171	173	90	20	88	5	49	5	52
	Romero et al.	7	Mean	380	120000	24000	22000	4800	3900	11*	1100	130	140	11	90	7	70
	Difference		Mean	-52%	-58%	-24%	-50%	-35%	-36%	5018%	-70%	-45%	-18%	-31%	12%	13%	-3%
Lower Loa	This work	29	Mean	342	90981	18841	14173	4250	5126	551	757	48	179	10	71	11	65
			SD	231	51130	6361	5021	1733	4004	174	496	36	32	5	29	3	26
			Max	863	228006	33202	26840	9097	15925	1059	1954	123	258	22	122	16	130
			Min	106	41991	7287	4725	2027	1697	351	254	14	117	5	22	4	21
	Romero et al.	13	Mean	700	125000	24000	23000	5900	5600	14*	1200	70	140	14	90	9	60
	Difference		Mean	-51%	-27%	-21%	-38%	-28%	-8%	3836%	-37%	-32%	28%	-26%	-21%	19%	9%
San Salvador	This work	12	Mean	604	124360	22481	25237	4471	6880	473	1181	1159	142	9	231	8	65
			SD	457	64027	20445	24139	3272	1322	83	248	1017	61	4	65	3	45
			Max	1954	290488	80381	86383	10596	9796	685	1391	3637	316	19	335	14	171
			Min	376	23010	9122	7869	1085	5063	335	623	447	93	4	112	1	35
	Romero et al.	2	Mean	250	86500	27000	18000	3600	2300	380	580	80	140	11	90	7	80
	Difference		Mean	141%	44%	-17%	40%	24%	199%	25%	104%	1348%	1%	-14%	156%	9%	-19%

the presence of Fe, while Loa and San Salvador samples are dominated by Ca. Other major sediment components such as Si, S and C were not measured.

Three of the samples with highest As concentrations were analyzed by XRD to determine their mineral composition. Results (Table 5-3) identified calcite, quartz, and aluminosilicates as the main solid phases present in these samples.

Two of the samples with the highest measured As contents (from Codelco A and Ayquina B) were found in thin layers of fine sediments with an orange color, suggesting a high content of Fe oxyhydroxides. Nevertheless, these samples do not show Fe concentrations higher than their adjacent strata. XRD analysis of the superficial Ayquina B sample showed no evidence for a Fe phase. Further sediment characterization is required to understand this behavior.

Table 5-3. Mineral phases identified by X-ray diffraction on three As-rich sediment samples.

Site	Identified phases
Sloman (4-5 cm)	Calcite (CaCO_3)
Quillagua (0-5 cm)	Quartz (SiO_2), Calcite (CaCO_3), Labradorite ($\text{Na}_{0.45}\text{Ca}_{0.55}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$)
Ayquina B (0-1 cm)	Quartz (SiO_2), Labradorite ($\text{Na}_{0.45}\text{Ca}_{0.55}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$), Albite ($\text{Na}(\text{Si}_3\text{Al})\text{O}_8$), Anorthite sodian ($\text{Na}_{0.45}\text{Ca}_{0.55}(\text{Al}_{1.55}\text{Si}_{2.45}\text{O}_8)$), Andesine ($\text{Na}_{0.685}\text{Ca}_{0.347}\text{Al}_{1.46}\text{Si}_{2.54}\text{O}_8$)

5.3. Elemental correlations in sediments

Table 5-4 shows that As is positively correlated at several sites with Sb, Cu, Mn, Ca, Na, B, and Sr, and negatively to Pb, Al, Co, and Cr. Pearson correlations with $|R| > 0.7$ and $p < 0.05$ were considered strong. No clear tendency in As correlation with Fe is observed.

Table 5-4. Correlation coefficients of selected chemical components with As for sediment cores from the Loa Basin (16 cores were analyzed).

Element	Number of cores with positive correlation ($R > 0.7$)	Number of cores with negative correlation ($R < -0.7$)	Tendency (positive or negative correlation)
Sb	6	2	+
Cu	7	1	+
Fe	2	4	
Mn	7	1	+
Ni	2	3	
Pb	1	4	-
Zn	2	2	
Ca	7	0	+
K	1	3	
Mg	2	1	
Na	7	0	+
Al	0	4	-
B	8	1	+
Ba	3	1	
Co	2	5	-
Cr	1	6	-
V	3	5	
Sr	10	0	+

Although Fe is present in water and sediments, and waters are supersaturated with respect to phases well known to sorb arsenate, such as goethite (FeOOH) (Wilkie & Hering, 1996; Dixit & Hering, 2003), the absence of any noticeable correlation between As and Fe suggests that this mechanism is not strongly operating. This may be caused by the elevated concentrations of competing ions, including dissolved silica (SiO_2) content in the waters, with values ranging from 20 mg/l Si in the Upper Loa to over 50 mg/l Si in the Salado River, which receives the Si-rich waters from the El Tatio hydrothermal discharges (Romero et al., 2003). Si concentrations below 10 mg/l have been shown to strongly hinder As removal from solution at mildly alkaline pH by sorption onto ferric hydroxides, through competition for sorption sites and lowering of surface potential

(Meng et al., 2000; Ruiping et al., 2007). A similar interference from silica on the removal of arsenate by adsorption has been observed for activated alumina (Clifford & Ghurye, 2002).

Correlation with Ca in sediments is likely to play a role in the immobilization of As. Arsenic incorporation into calcite crystal lattices has been recently suggested to pose a limit on As mobility under conditions where immobilization through sorption onto metal oxides is not important (Di Benedetto et al., 2006; Alexandratos et al., 2007; Sørensen et al., 2008), as it appears to be the case in this system.

Sorption onto calcite should not be inhibited by the high concentrations of silicate, which does not adsorb significantly onto carbonates (Mayer & Gloss, 1980). The high correlation of Ca with Mn and Sr could be related to the incorporation of these onto calcite minerals (substitution of Mn^{2+} or Sr^{2+} for Ca^{2+}), forming solid solutions with the form $\text{Me}_{(x)}\text{Ca}_{(1-x)}\text{CO}_3$ (where Me is any divalent metal) as described by Billon et al. (2002).

5.4. Selected study site: Loa at Sloman Reservoir

This site was selected for a more detailed analysis for several reasons. A dam was built on this part of the river in the 1920s with the purpose of electricity generation for the saltpeter mining industry, the main economic activity in the area at that time. Since then, sediments have been accumulating in the reservoir. Extremely elevated As concentrations in reservoir waters (up to 30 mg/l) have been reported during flood events, with great impact on the fluvial and marine ecosystems downstream, as well as on the supply of water for human activities (Arroyo et al., 1999). The flood event occurred in 2001 increased the flow in the Loa River near Calama in more than two orders of magnitude, from a base flow of 1.7 m³/s to over 200 m³/s. The last important flood was reported in 2006, with flows of up to 30 m³/s.

Close vicinity downstream of the Quillagua oasis village and the fact that it is the last reservoir before the outlet to the Pacific Ocean make the Sloman Reservoir particularly important: water quality exiting the reservoir will affect crops in the village and marine wildlife near the outlet, main subsistence resource for small communities in the surrounding coastal area.

The sediment core taken at this site in June 2007 was visibly divided onto three strata (Figure 5-3 A), all of them composed of fine material: a pale orange top stratum (0-3.5 cm depth), followed by a pale brown/yellow stratum (3.5-7 cm depth) and a darker brown stratum (7-13 cm depth). Elemental composition of the sediments as determined by aqua regia extraction and ICP-AES analysis shows that the central stratum has a higher content of As, Ca, Mn and Na, and a lower content of Al, Co, Cr, Cu, Fe, K, Mg, Ni, Pb, and Zn, relative to the upper and lower strata. No clear stratification is observed for B, Ba, or Sb contents. Table 5-5 shows the correlation coefficients of the measured elements with As.

Table 5-5. Correlation coefficients (R) for As with selected elements for a sediment core taken from the Sloman Reservoir in the Loa River (Core A).

Element	Cu	Fe	Mn	Zn	Ca	K	Mg	Na	Al	B	Cr	Sr
R	-0.70	-0.78	0.89	-0.70	0.90	-0.90	-0.74	0.30	-0.88	-0.44	-0.94	0.87

Mn, Ca, and Sr are strongly correlated to As in the sediment samples. Figure 5-4 shows profiles for As, Fe Ca, Sr and Mn in this core.

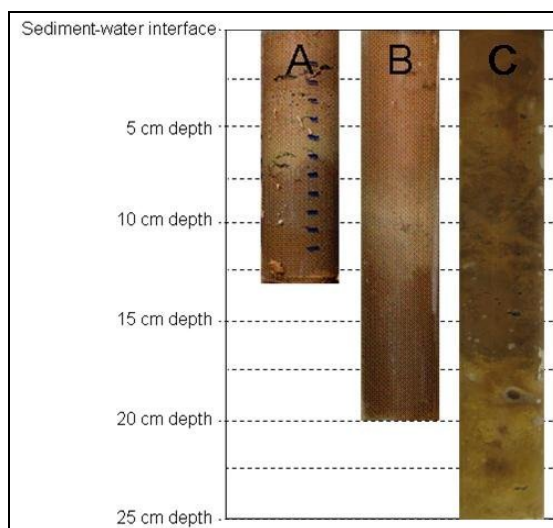


Figure 5-3. Sediment cores taken from the Sloman Reservoir in the Loa River. **A:** June 2007. **B** and **C:** July 2008.

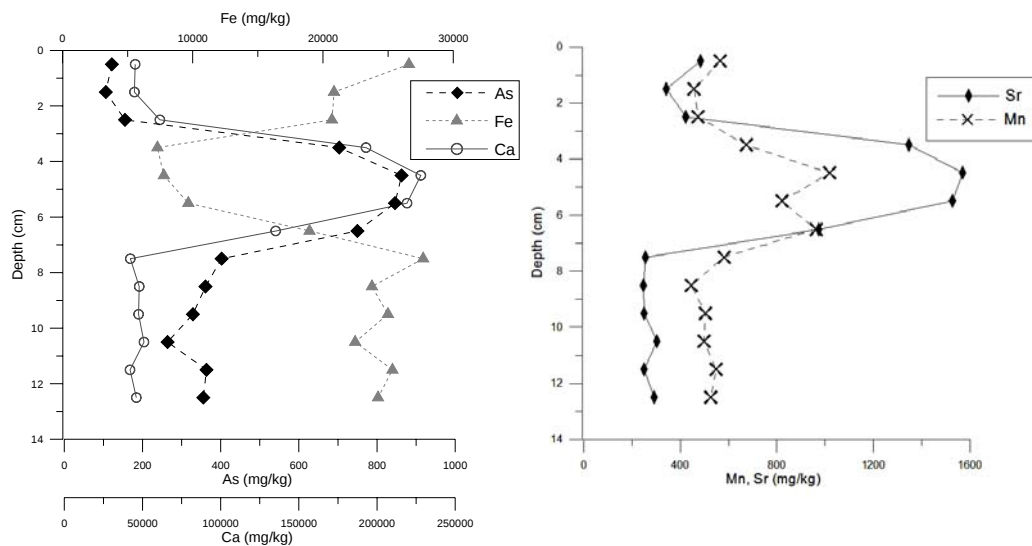


Figure 5-4. As, Fe, Ca, Mn and Sr content profiles for a sediment core taken from the Sloman Reservoir in the Loa River (Core A).

Samples from the three strata were analyzed by Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry (SEM-EDS), to obtain additional composition information, as well as spatial distribution of the elements, trying to identify the dominating mineral forms and possible As-rich particles. The sample from the first stratum (1-2 cm) showed spatially correlated concentrations of Al, Si, O, and Mg, suggesting the presence of aluminosilicates. The presence of KCl and CaSO₄ are also suggested by the molar ratios and spatial correlation between K and Cl, and between Ca and S, respectively. Fe appears scattered over the whole sample area. The sample from the second stratum (5-6 cm) exhibits high Ca, O, and C contents, suggesting CaCO₃ presence. Important concentrations for Al, Si, Fe and S were found scattered throughout the sample. The sample from the third stratum (10-11 cm) showed elevated Si and Al contents, suggesting the dominance of aluminosilicates. Ca and Mg are found scattered throughout the sample. Relatively high Fe concentration (1.8% atomic weight basis) is present, located at specific areas of the samples, indicating Fe-rich particles. No presence of As was detected in any of the analyzed samples. This is likely due to the fact that As is a minor component in these sediments, comprising less than 0.1% of their weight.

This SEM-EDS analysis is consistent with the observation of three strata in the sediment profile. While the first and third strata appear to be mainly composed of clay minerals, the middle stratum has a significantly different composition, with an important contribution of Ca and C, consistent with XRD identification of calcite in the same sample. This middle stratum could correspond to a massive sediment transport episode, related to a flood event, in which alluvial sediments could have entered the fluvial system and settled in the Sloman Reservoir. Hierarchical clustering of the samples also supports this hypothesis, showing clearly the presence of three strata (Figure 5-5). The top and bottom strata are three times statistically more similar between them than to the middle stratum, suggesting a different source.

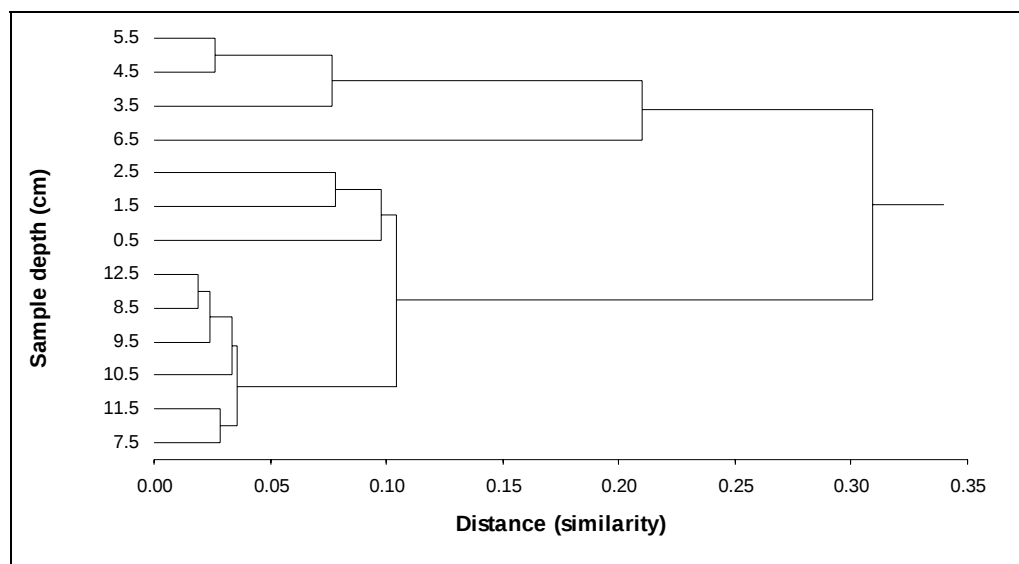


Figure 5-5. Data clustering considering elemental compositions for samples from a sediment core taken from the Sloman Reservoir in the Loa River. Distance in the x-axis is a measure of the similarity between samples (Core A).

In July 2008, two more sediment cores (Figure 5-3 B and C) were extracted at the same sampling point, approximately 1 m apart from the 2007 sampling site. Core B showed exactly the same strata seen in Core A, with the difference that the first stratum is approximately 4 cm deeper. This could give an approximate sedimentation rate for a regular year, with no major flood events. Core C, on the other hand, presents the same strata, but in a more disorderly fashion. In addition, for it is deeper than the previous cores, it shows an additional pale stratum in the bottom.

The sequential extraction procedure was applied to Core C, sectioned every 2.5 cm. Results (

Figure 5-6) show a similar stratification in total As content to those found in Core A from the previous year. Higher concentrations found in the top stratum, relative to Core A, suggest possible upward diffusion of As from the middle layer, where it is found in a very labile form, 80% of it being extracted in the first step of the procedure, which

targets ionically bound As (Table 4-2). During this upward flux, the higher abundance of particles with affinity for As, such as Fe oxyhydroxides, could explain the higher extraction percentages associated with the second fraction, targeting strongly adsorbed As.

The As found in the recently deposited top sediment section (0-2.5 cm) is mostly ionically bound (Mg step). In the following sections, the ionically bound fraction loses importance with respect to the strongly adsorbed fraction (PO₄ step), suggesting the modification of binding mechanisms within the sediment with time.

Under 10% of As in sediments is found in the third (HCl) step, which targets As coprecipitated with Mn oxides, very amorphous Fe oxyhydroxides, carbonates, and acid volatile sulfides. The release of Fe into solution at this step indicates the presence of amorphous Fe oxyhydroxides, which could have coprecipitated As as a minor component, though this is clearly not a dominating As phase in these sediments. The dissolution of calcite, which is targeted by this step, does not seem to release considerable amounts of As, which renders surface complexation (targeted in the PO₄ step) rather than coprecipitation a more likely mechanism for As association with calcite.

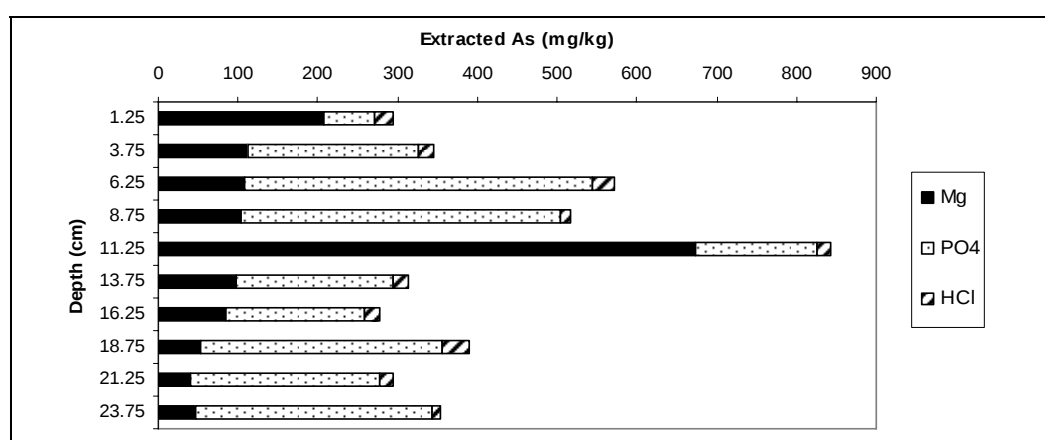


Figure 5-6. Arsenic extracted by each phase of the sequential extraction procedure for a sediment core taken from the Sloman Reservoir in the Loa River (Core C).

PHREEQC software (Parkhurst & Appelo, 1999) was used to calculate the speciation of As for the Sloman Reservoir waters, using the data obtained for this site (Table 5-1). Additional water chemistry data was taken from Romero et al. (2003) (Eh=0.43 V, Alkalinity=420 mg/l, $[\text{SO}_4^{2-}]$ =720 mg/l, $[\text{SiO}_2]$ =50 mg/l). The Wateq4f database was used, with the addition of the equations for the formation of aqueous and solid calcium arsenates compiled by Alexandratos et al. (2007), listed in Table 5-6.

Table 5-6. Data used for modeling of aqueous and solid calcium arsenates (Alexandratos et al., 2007).

Reaction	logK
$\text{CaAsO}_4^- = \text{Ca}^{2+} + \text{AsO}_4^{3-}$	-4.36
$\text{CaHAsO}_4 = \text{Ca}^{2+} + \text{HAsO}_4^{2-}$	-2.66
$\text{CaH}_2\text{AsO}_4^+ = \text{Ca}^{2+} + \text{H}_2\text{AsO}_4^-$	-1.30
$\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2(\text{H}_2\text{O})_{4(s)} = 4\text{Ca}^{2+} + 2\text{AsO}_4^{3-} + 2\text{OH}^- + 4\text{H}_2\text{O}$	-29.20
$\text{Ca}_5(\text{AsO}_4)_3\text{OH}_{(s)} = 5\text{Ca}^{2+} + 3\text{AsO}_4^{3-} + \text{OH}^-$	-38.04
$\text{Ca}_3(\text{AsO}_4)_2(\text{H}_2\text{O})_{4(s)} = 3\text{Ca}^{2+} + 2\text{AsO}_4^{3-} + 4\text{H}_2\text{O}$	-21.00
$\text{CaHAsO}_4(\text{H}_2\text{O})_{(s)} = \text{Ca}^{2+} + \text{HAsO}_4^{2-} + \text{H}_2\text{O}$	-4.79

Table 5-7. Saturation indexes for calcium arsenates and calcite obtained for Sloman Reservoir water data.

Mineral phase	Saturation Index
$\text{Ca}_3(\text{AsO}_4)_2(\text{H}_2\text{O})_4$	-3.82
$\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2(\text{H}_2\text{O})_4$	-10.17
$\text{Ca}_5(\text{AsO}_4)_3\text{OH}$	-6.45
$\text{CaHAsO}_4(\text{H}_2\text{O})$	-2.93
Calcite (CaCO_3)	1.57

The solution was found to be undersaturated for As-bearing minerals, including solid calcium arsenates (Table 5-7), therefore, it is unlikely that As in waters is limited by solubility. The solution is oversaturated with respect to calcite, consistent with high Ca concentration in sediments and results from XRD analysis.

According to equilibrium calculations, the dominating As species in solution in the Sloman reservoir would be HAsO_4^{2-} (Table 5-8). It is interesting to note that more than 30% of the As in solution is present as the uncharged calcium arsenate species CaHAsO_4 . This uncharged species, unlike HAsO_4^{2-} , probably will not have a high affinity for sorption onto positively charged surfaces and will thus be highly mobile.

A positive correlation between the calculated activity of CaHAsO_4 and the amount of As(V) adsorbed onto calcite has been reported for batch experiments (Sørensen et al., 2008), but there is no direct evidence for this species controlling As sorption onto calcite.

Table 5-8. Arsenic speciation in waters of the Sloman Reservoir obtained by PHREEQC modeling.

Species	Concentration (μM)	% of total As species
HAsO_4^{2-}	16.1	63.4
CaHAsO_4	8.5	33.5
H_2AsO_4^-	0.5	2.1
CaAsO_4^-	0.2	0.8

As(III) species are negligible according to these calculations, nevertheless, it is likely they are present to some degree because of microbial activity (Oremland & Stolz, 2003), which is yet to be assessed for this system. Sørensen et al. (2008) found As(V) to be strongly adsorbed on calcite, unlike As(III). Therefore, change in redox conditions may strongly

affect As mobility in calcite-rich sediments. This could play a role in the Sloman Reservoir during unusual flood events where anoxic conditions have been reported to develop. As(V) could be reduced to As(III) and therefore desorbed and liberated to the water column.

Nevertheless, Román-Ross et al. (2006) found arsenite to sorb onto and co-precipitate with calcite. Their results show that in a system where calcite is precipitating in the presence of high As(III) concentrations, an average concentration of 30 ± 6 mmol/kg of As (III) could be incorporated into calcite structure.

Alexandratos et al. (2007) studied As(V) uptake by calcite. Sorption experiments at pH=8.3 gave a maximum capacity of 6.5 mmol As/kg CaCO_3 after 24 hours of equilibration in a calcite-saturated solution. They recognize that this capacity could be significantly higher over longer timescales, owing to slower processes such as coprecipitation, surface precipitation and diffusion to less accessible sites. This could be the case at reservoirs with an important hydraulic retention time, or at the sediment/porewater interface.

A previous study (Le Guern et al., 2003) reported that calcite played only a minor role on As trapping in an experimental setting using water from a geothermal spring (0.14 mmol As/kg CaCO_3 .) The As concentration they used (0.04 mg/l) was two orders of magnitude lower than the one measured at Sloman (1.9 mg/l). In addition, the alkalinity of the water they used was significantly higher than the one reported for the Sloman Reservoir (6 g/l vs. 420 mg/l). Carbonate is believed to compete with As oxyanions for sorption sites on the calcite surface (Sø et al., 2008). These differences in water composition may account for the dissimilar incorporation of As to calcite in both systems.

Figure 5-7 shows the ratio of As to calcite in Core A, assuming that all the Ca measured in the sediment is present in this mineral phase. For the upper two strata, the ratio lies between reported calcite capacities to immobilize As(V) and As(III). This could be interpreted as a) sorption/incorporation of As(III) on calcite, b) higher incorporation of As(V) onto calcite than reported values, presumably due to longer contact times, or c) a combination of both.

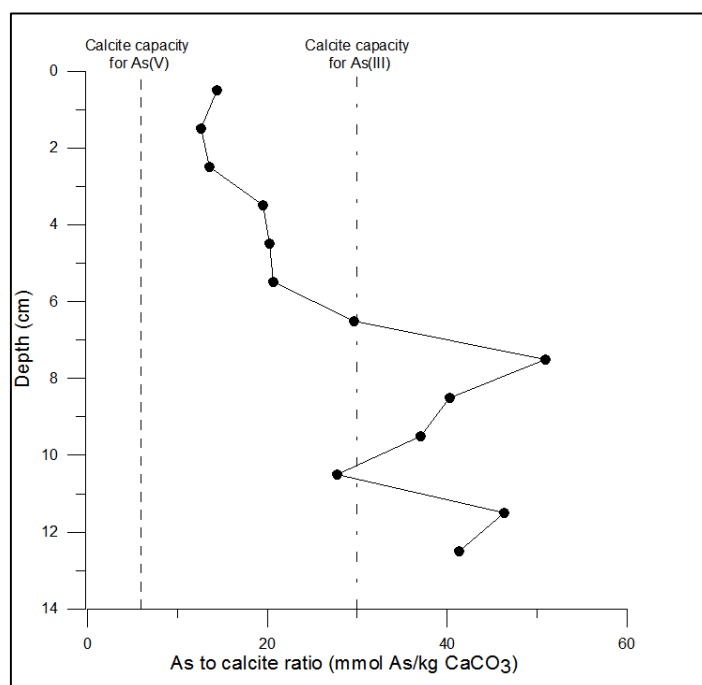


Figure 5-7. Arsenic to calcite ratio for sediment samples from the Sloman Reservoir (Core A). Calculations assume that all of the sediment Ca is present as calcite. Dashed lines show reported capacities of calcite for incorporation reported for As(V) (Alexandratos et al., 2007) and As(III) (Román-Ross et al., 2006).

Cores from Salado Baden and Loa Cruce A, which also show a high degree of correlation between Ca, As, Sr and Mn (all negatively correlated to Fe), show similar ratios, ranging from 10 to 21 mmol As/kg CaCO₃, suggesting a maximum capacity of calcite for As under these environmental conditions. The higher ratio observed for

deeper sediments in the Sloman Reservoir (Figure 5-7) indicate a presence of a different As-bearing phase, possibly favored by reducing conditions.

6. CONCLUSIONS

Results from water analyses are consistent with previous reports, thus supporting the importance of the Tatio Geysers geothermal field As input to the Salado River, and the relevance of evaporation in the system. The water quality seems to be stable in time, with the exception of occasional major flood events during the summer, which are likely to transport considerable amounts of sediment to the rivers.

Arsenic concentrations in vertical sediment profiles show no common tendency throughout the basin, though some trends are observed at several points, such as As-rich sediments in the top layers. The highest average As contents are found in the San Salvador Wetland (604 mg/kg), the Salado River (414 mg/kg), and the Lower Loa (342 mg/kg).

The identification of a groundwater spring rich in As, Fe, Cu, and other metals and their entrapment in the sediments in the wetland at the head of the San Salvador River suggest mining activity in the area to be an input of these elements to the system.

There is no evidence for a Fe oxyhydroxide controlled deposition of As in the sediments, which is often the case in aerobic waters. The correlation between As and Ca contents and the evidence for the presence of calcite in the sediments suggest that this mineral may play a key role in the As cycling in the system through coprecipitation and adsorption of As species.

Sequential extraction results for Sloman Reservoir, a site of massive sediment accumulation in the Loa River, show that As is mostly found either ionically bound or strongly adsorbed to carrier phases, and remains present in these labile phases even at depths under 20 cm, thus available for eventual remobilization to the water column. The

elevated labile concentrations at this site may explain the fact that it shows the highest dissolved As concentrations in all of the Lower Loa River.

Evident stratification at this site suggests the deposition of As-rich calcite particles during flood events. The As-binding mechanisms in these sediments should be further studied by direct speciation techniques, such as X-ray absorption spectroscopy (XAS). Analysis of deeper sediment cores (up to tens of meters), including radioisotope dating techniques, could help reconstruct the history of sediment deposition and gain valuable knowledge about the processes and sources involved in the cycling of As and other pollutants in the basin.

Further characterization in the watershed is suggested to determine the main controls on As in the system, including groundwater and porewater sampling, and X-ray absorption spectroscopy, X-ray diffraction and sequential extraction analyses on sediments.

Recent research has identified calcite as a potential sink for As under industrial and laboratory conditions, through different processes that are yet to be clearly established. This study gives evidence that indicates that these processes are relevant in the Loa River Basin, making it a model site for their study under arid, alkaline environmental conditions.

7. IMPLICATIONS AND FUTURE PERSPECTIVES

The information retrieved by this work contributes to further characterize the geochemistry of the Loa River Basin. Because of the high variability in mineralogical, chemical and hydrological conditions throughout the basin, the distribution and associations of As are heterogeneous. It is clear that surface sediments analyses are not enough to assess As presence in the sediments, since depth distribution is highly variable.

The main finding in this work is the fact that As does not appear to be largely controlled by Fe or Mn oxyhydroxides in this watershed. Evidence suggests that calcite may play a key role, but it is likely that other relevant mechanisms controlling As cycling remain largely unknown, requiring further investigation for their understanding. This poses an opportunity for further research, which will help to understand the complex interaction of mechanisms involved. The results of this work hint directions for the application of more specific analyses, such as:

- X-ray absorption spectroscopy (XAS): this technique may allow identifying of the characteristics of As coordination in mineral phases.
- Sediment texture analysis: coupled with geologic information from the basin, it may help understand the source of specific sediments and the conditions necessary for their transport.
- Sediment porewater analysis: determination of dissolved constituents such as As(III), As(V), Fe(II), Fe(III) as S(-II), coupled to bulk sediment composition, may shed light on the redox controls and sediment/porewater interactions.

- Radioisotope sediment dating: determination of the age of sediments may help to understand the sources of As and other contaminant input to the sediments, such as flood events or anthropogenic activities.
- Identification of biotic interactions: plants or microorganisms may exert controls on As mobility and speciation.

REFERENCES

- Alexandratos, V. G., Elzinga, E. J., & Reeder, R. J. (2007). Arsenate uptake by calcite: macroscopic and spectroscopic characterization of adsorption and incorporation mechanisms. *Geochimica et Cosmochimica Acta* **71**, 4172-4187.
- Arroyo, A., Alonso, H., Vera, L., & Ortega, P. (1999). Análisis de los eventos ocurridos en Río Loa marzo de 1997. *XIII Congreso de Ingeniería Sanitaria y Ambiental AIDIS*. Antofagasta, Chile.
- Billon, G., Ouddane, B., Recourt, P., & Boughriet, A. (2002). Depth variability and some geochemical characteristics of Fe, Mn, Ca, Mg, Sr, S, P, Cd and Zn in anoxic sediments from Authie Bay (northern France). *Estuarine, Coastal and Shelf Science* **55**, 167-181.
- Bostick, B. C., Chen, C., & Fendorf, S. (2004). Arsenite retention mechanisms within estuarine sediments of Pescadero, CA. *Environmental Science & Technology* **38**, 3299-3304.
- Bostick, B. C., & Fendorf, S. (2003). Arsenite sorption on troilite (FeS) and pyrite (FeS₂). *Geochimica et Cosmochimica Acta* **67**, 909-921.
- Cáceres, D. D., Pino, P., Montesinos, N., Atalah, E., Amigo, H., & Loomis, D. (2005). Exposure to inorganic arsenic in drinking water and total urinary arsenic concentration in a Chilean population. *Environmental Research* **98**, 151-159.
- Clifford, D. A., & Ghurye, G. L. (2002). Metal-oxide adsorption, ion exchange, and coagulation-microfiltration for arsenic removal from water. In W. T. Frankenberger (Ed.), *Environmental Chemistry of Arsenic* (pp. 217-245). New York: Marcel Dekker.
- Di Benedetto, F., Costagliola, P., Benvenuti, M., Lattanzi, P., Romanelli, M., & Tanelli, G. (2006). Arsenic incorporation in natural calcite lattice: evidence from electron spin echo spectroscopy. *Earth and Planetary Science Letters* **246**, 458-465.

- Dixit, S., & Hering, J. G. (2003). Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environmental Science & Technology* **37**, 4182-4189.
- Ferreccio, C., & Sancha, A. M. (2006). Arsenic exposure and its impact on health in Chile. *Journal of Health Population and Nutrition* **24**, 164-175.
- Francesconi, K. A., & Kuehnelt, D. (2002). Arsenic compounds in the environment. In W. T. Frankenberger (Ed.), *Environmental Chemistry of Arsenic* (pp. 51-94). New York: Marcel Dekker.
- Frankenberger, W. T. (2002). Preface. In W. T. Frankenberger (Ed.), *Environmental Chemistry of Arsenic* (pp. iii-v). New York: Marcel Dekker.
- García-Manyes, S., Jiménez, G., Padro, A., Rubio, R., & Rauret, G. (2002). Arsenic speciation in contaminated soils. *Talanta* **58**, 97-109.
- Harvey, C. F., Swartz, C. H., Badruzzaman, A. B. M., Keon-Blute, N., Yu, W., Ali, M. A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P. M., Ashfaq, K. N., Islam, S., Hemond, H. F., & Ahmed, M. F. (2002). Arsenic mobility and groundwater extraction in Bangladesh. *Science* **298**, 1602-1606.
- Hering, J. G., & Kneebone, P. E. (2002). Biogeochemical controls on arsenic in water. In W. T. Frankenberger (Ed.), *Environmental Chemistry of Arsenic* (pp. 155-181). New York: Marcel Dekker.
- Hopenhayn-Rich, C., Browning, S. R., Hertz-Picciotto, I., Ferreccio, C., Peralta, C., & Gibb, H. (2000). Chronic arsenic exposure and risk of infant mortality in two areas of Chile. *Environmental Health Perspectives* **108**, 667-673.
- Huerta-Díaz, M. A., Tessier, A., & Carignan, R. (1998). Geochemistry of trace metals associated with reduced sulfur in freshwater sediments. *Applied Geochemistry* **13**, 213-233.
- Inskip, W. P., McDermott, T. R., & Fendorf, S. (2002). Arsenic (V)/(III) cycling in soils and natural waters: chemical and microbiological processes. In W. T.

Frankenberger (Ed.), *Environmental Chemistry of Arsenic* (pp. 183-215). New York: Marcel Dekker.

ISO. (1995). Standard 11466. Soil quality - Extraction of trace metals soluble in aqua regia.

Jay, J. A., Blute, N. K., Lin, K., Senn, D., Hemond, H. F., & Durant, J. L. (2005). Controls on arsenic speciation and solid-phase partitioning in the sediments of a two-basin lake. *Environmental Science & Technology* **39**, 9174-9181.

Keimowitz, A. R., Zheng, Y., Chillrud, S. N., Mailloux, B., Jung, H. B., Stute, M., & Simpson, H. J. (2005). Arsenic redistribution between sediments and water near a highly contaminated source. *Environmental Science & Technology* **39**, 8606-8613.

Keon, N. E., Swartz, C. H., Brabander, D. J., Harvey, C., & Hemond, H. F. (2001). Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environmental Science & Technology* **35**, 2778-2784.

Kneebone, P. E., O'Day, P. A., Jones, N., & Hering, J. G. (2002). Deposition and fate of arsenic in iron- and arsenic-enriched reservoir sediments. *Environmental Science & Technology* **36**, 381-386.

Le Guern, C., Baranger, P., Crouzet, C., Bodenan, F., & Conil, P. (2003). Arsenic trapping by iron oxyhydroxides and carbonates at hydrothermal spring outlets. *Applied Geochemistry* **18**, 1313-1323.

Loska, K., & Wiechula, D. (2006). Comparison of sample digestion procedures for the determination of arsenic in bottom sediment using hydride generation AAS. *Microchimica Acta* **154**, 235-240.

Martin, A. J., & Pedersen, T. F. (2002). Seasonal and interannual mobility of arsenic in a lake impacted by metal mining. *Environmental Science & Technology* **36**, 1516-1523.

May, G., Hartley, A. J., Stuart, F. M., & Chong, G. (1999). Tectonic signatures in arid continental basins: an example from the Upper Miocene-Pleistocene, Calama

Basin, Andean forearc, northern Chile. *Palaeogeography, Palaeoclimatology, Palaeoecology* **151**, 55-77.

Mayer, L. M., & Gloss, S. P. (1980). Buffering of silica and phosphate in a turbid river. *Limnology and Oceanography* **25**, 12-22.

McNeill, L. S., Chen, H. W., & Edwards, M. (2002). Aspects of arsenic chemistry in relation to occurrence, health and treatment. In W. T. Frankenberger (Ed.), *Environmental Chemistry of Arsenic* (pp. 141-153). New York: Marcel Dekker.

Meng, X., Bang, S., & Korfiatis, G. P. (2000). Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. *Water Research* **34**, 1255-1261.

Moore, J. N., Ficklin, W. H., & Johns, C. (1988). Partitioning of arsenic and metals in reducing sulfidic sediments. *Environmental Science & Technology* **22**, 432-437.

Nicholas, D. R., Ramamoorthy, S., Palace, V., Spring, S., Moore, J. N., & Rosenzweig, R. F. (2003). Biogeochemical transformations of arsenic in circumneutral freshwater sediments. *Biodegradation* **14**, 123-137.

O'day, P. A., Vlassopoulos, D., Root, R., & Rivera, N. (2004). The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proceedings of the National Academy of Sciences of the United States of America* **101**, 13703-13708.

Oremland, R. S., & Stolz, J. F. (2003). The ecology of arsenic. *Science* **300**, 939-944.

Parkhurst, D. L., & Appelo, C. A. J. (1999). User's Guide to PHREEQC, version 2. *U.S. Geological Survey Water Resource Inv.* 99-4259.

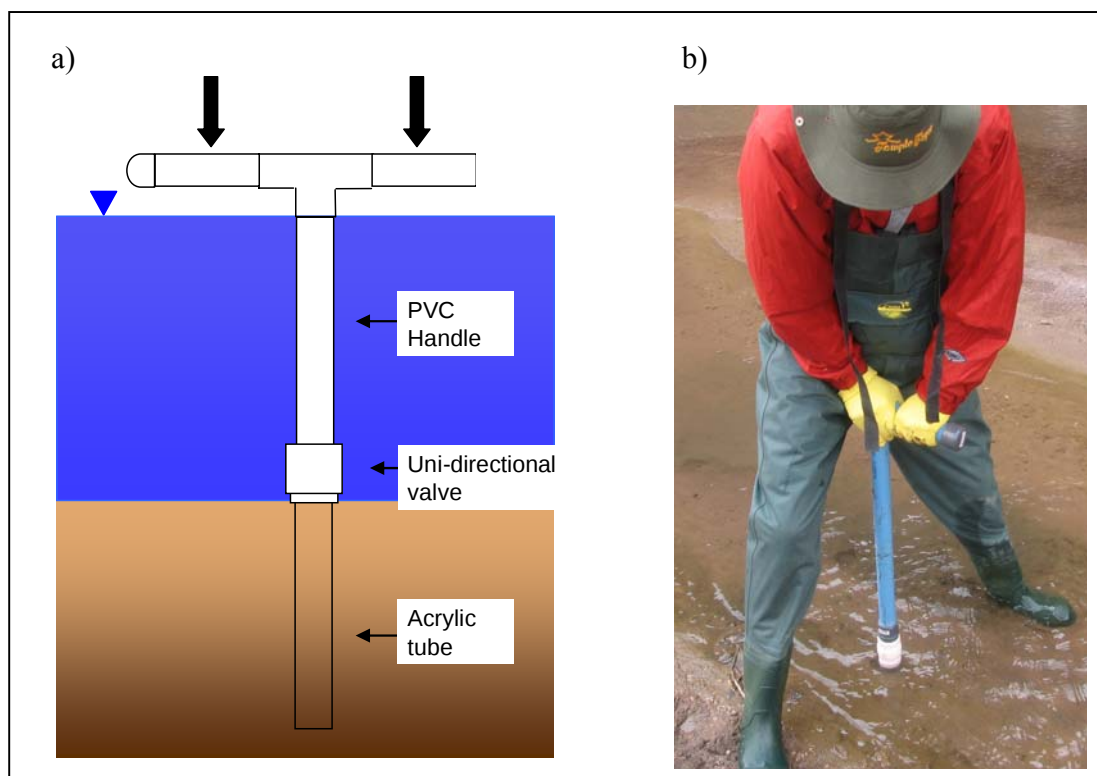
Peltier, E., Dahl, A. L., & Gaillard, J. F. (2005). Metal speciation in anoxic sediments: When sulfides can be construed as oxides. *Environmental Science & Technology* **39**, 311-316.

- Pizarro, I., Gomez, M. M., Camara, C., & Palacios, M. A. (2003). Distribution of arsenic species in environmental samples collected in Northern Chile. *International Journal of Environmental Analytical Chemistry* **83**, 879-890.
- Postma, D., Larsen, F., Hue, N. T. M., Duc, M. T., Viet, P. H., Nhan, P. Q., & Jessen, S. (2007). Arsenic in groundwater of the Red River floodplain, Vietnam: controlling geochemical processes and reactive transport modeling. *Geochimica et Cosmochimica Acta* **71**, 5054-5071.
- Queirolo, F., Stegen, S., Mondaca, J., Cortés, R., Rojas, R., Contreras, C., Muñoz, L., Schwuger, M. J., & Ostapczuk, P. (2000a). Total arsenic, lead, cadmium, copper, and zinc in some salt rivers in the northern Andes of Antofagasta, Chile. *Science of the Total Environment* **255**, 85-95.
- Queirolo, F., Stegen, S., Restovic, M., Paz, M., Ostapczuk, P., Schwuger, M. J., & Muñoz, L. (2000b). Total arsenic, lead, and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. *Science of the Total Environment* **255**, 75-84.
- Rapin, F., Tessier, A., Campbell, P. G. C., & Carignan, R. (1986). Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure. *Environmental Science & Technology* **20**, 836-840.
- Reynolds, J. G., Naylor, D. V., & Fendorf, S. E. (1999). Arsenic sorption in phosphate-amended soils during flooding and subsequent aeration. *Soil Science Society of America Journal* **63**, 1149-1156.
- Roberts, A., & Withers, P. (2007). StatistiXL (Version 1.7). Broadway - Nedlands, Western Australia.
- Román-Ross, G., Cuello, G. J., Turrillas, X., Fernández-Martínez, A., & Charlet, L. (2006). Arsenite sorption and co-precipitation with calcite. *Chemical Geology* **233**, 328-336.

- Romero, L., Alonso, H., Campano, P., Fanfani, L., Cidu, R., Dadea, C., Keegan, T., Thornton, I., & Farago, M. (2003). Arsenic enrichment in waters and sediments of the Río Loa (Second Region, Chile). *Applied Geochemistry* **18**, 1399-1416.
- Ruiping, L., Xing, L., Shengji, X., Yanling, Y., Rongcheng, W., & Guibai, L. (2007). Calcium-enhanced ferric hydroxide co-precipitation of arsenic in the presence of silicate. *Water Environment Research* **79**, 2260-2264.
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* **17**, 517-568.
- Smith, A. H., Arroyo, A. P., Mazumder, D. N. G., Kosnett, M. J., Hernandez, A. L., Beeris, M., Smith, M. M., & Moore, L. E. (2000). Arsenic-induced skin lesions among Atacameño people in Northern Chile despite good nutrition and centuries of exposure. *Environmental Health Perspectives* **108**, 617-620.
- Smith, A. H., Goycolea, M., Haque, R., & Biggs, M. L. (1998). Marked increase in bladder and lung cancer mortality in a region of Northern Chile due to arsenic in drinking water. *American Journal of Epidemiology* **147**, 660-669.
- Smith, A. H., Hoppenhaynrich, C., Bates, M. N., Goeden, H. M., Hertzpicciotto, I., Duggan, H. M., Wood, R., Kosnett, M. J., & Smith, M. T. (1992). Cancer risks from arsenic in drinking-water. *Environmental Health Perspectives* **97**, 259-267.
- Sø, H. U., Postma, D., Jakobsen, R., & Larsen, F. (2008). Sorption and desorption of arsenate and arsenite on calcite. *Geochimica et Cosmochimica Acta* **72**, 5871-5884.
- Tighe, M., Lockwood, P., Wilson, S., & Lisle, L. (2004). Comparison of digestion methods for ICP-OES analysis of a wide range of analytes in heavy metal contaminated soil samples with specific reference to arsenic and antimony. *Communications in Soil Science and Plant Analysis* **35**, 1369-1385.
- Van Herreweghe, S., Swennen, R., Vandecasteele, C., & Cappuyns, V. (2003). Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. *Environmental Pollution* **122**, 323-342.

- Welch, A. H., Westjohn, D. B., Helsel, D. R., & Wanty, R. B. (2000). Arsenic in ground water of the United States: occurrence and geochemistry. *Ground Water* **38**, 589-604.
- WHO. (2006). *Guidelines for drinking-water quality* (Third ed. Vol. 1 - Recommendations). Geneva: World Health Organization.
- Wilkie, J. A., & Hering, J. G. (1996). Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **107**, 97-110.
- Wilkin, R. T., Wallschläger, D., & Ford, R. G. (2003). Speciation of arsenic in sulfidic waters. *Geochemical Transactions* **4**, 1-7.
- Wolthers, M., Charlet, L., Van der Weijden, C. H., Van der Linde, P. R., & Rickard, D. (2005). Arsenic mobility in the ambient sulfidic environment: sorption of arsenic(V) and arsenic(III) onto disordered mackinawite. *Geochimica et Cosmochimica Acta* **69**, 3483-3492.

APPENDIXES

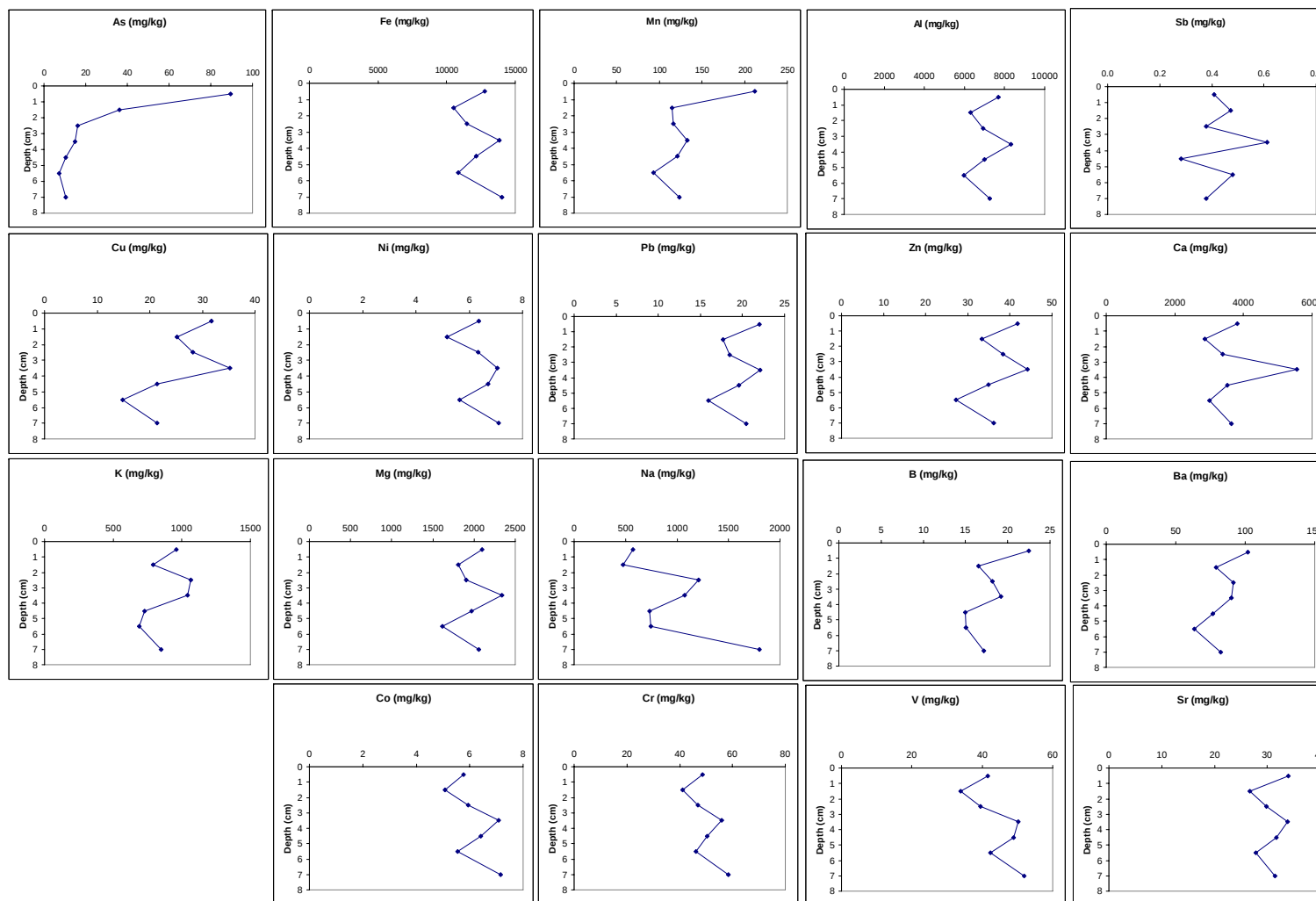
APPENDIX A: Sampling apparatus

a) Sediment corer scheme. b) Sediment corer in use in the Salado River.

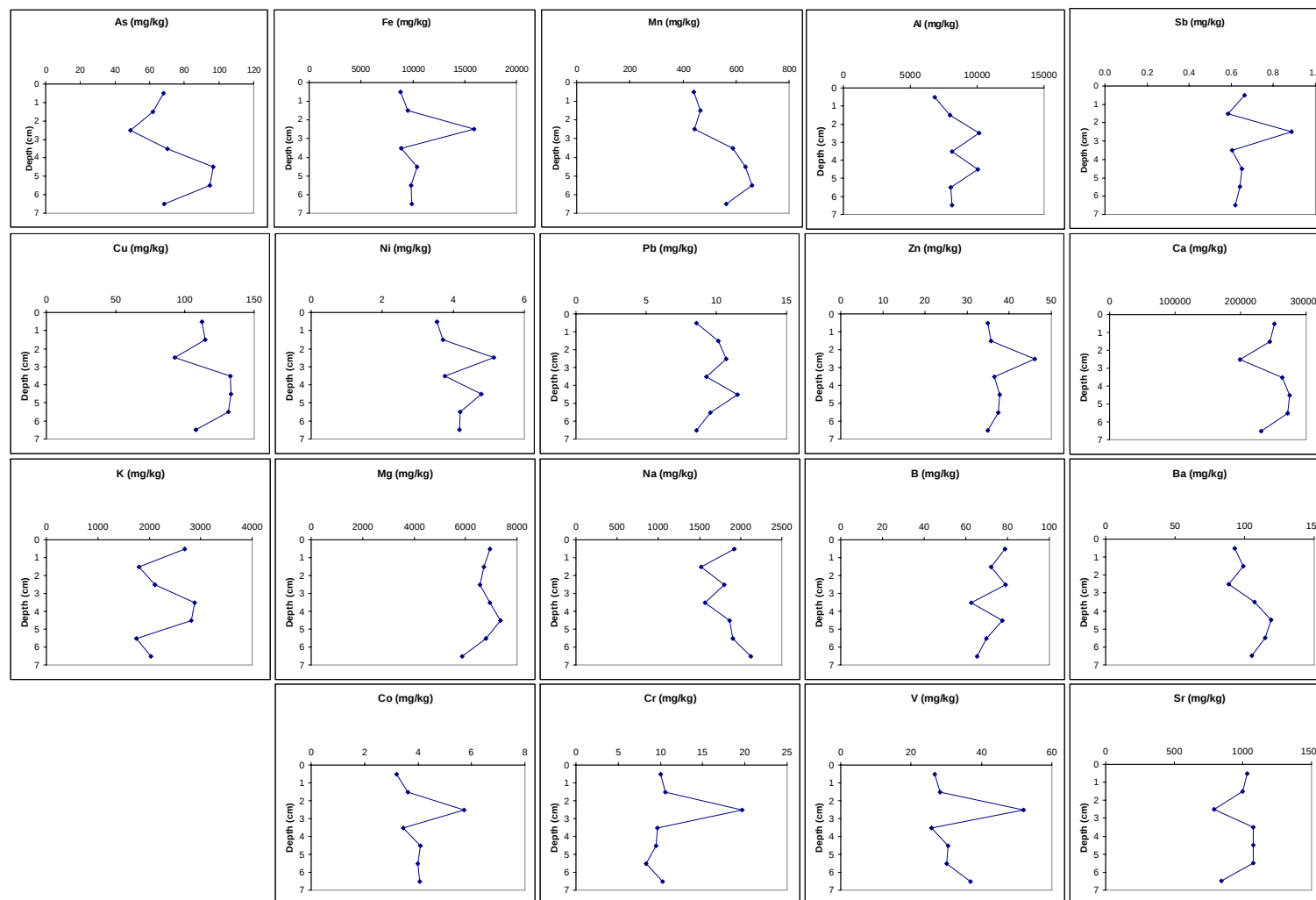
APPENDIX B: Sediment concentration profiles

This section shows sediment concentration profiles of selected chemical components for all the analyzed cores. Concentrations are plotted for the middle depth of each increment.

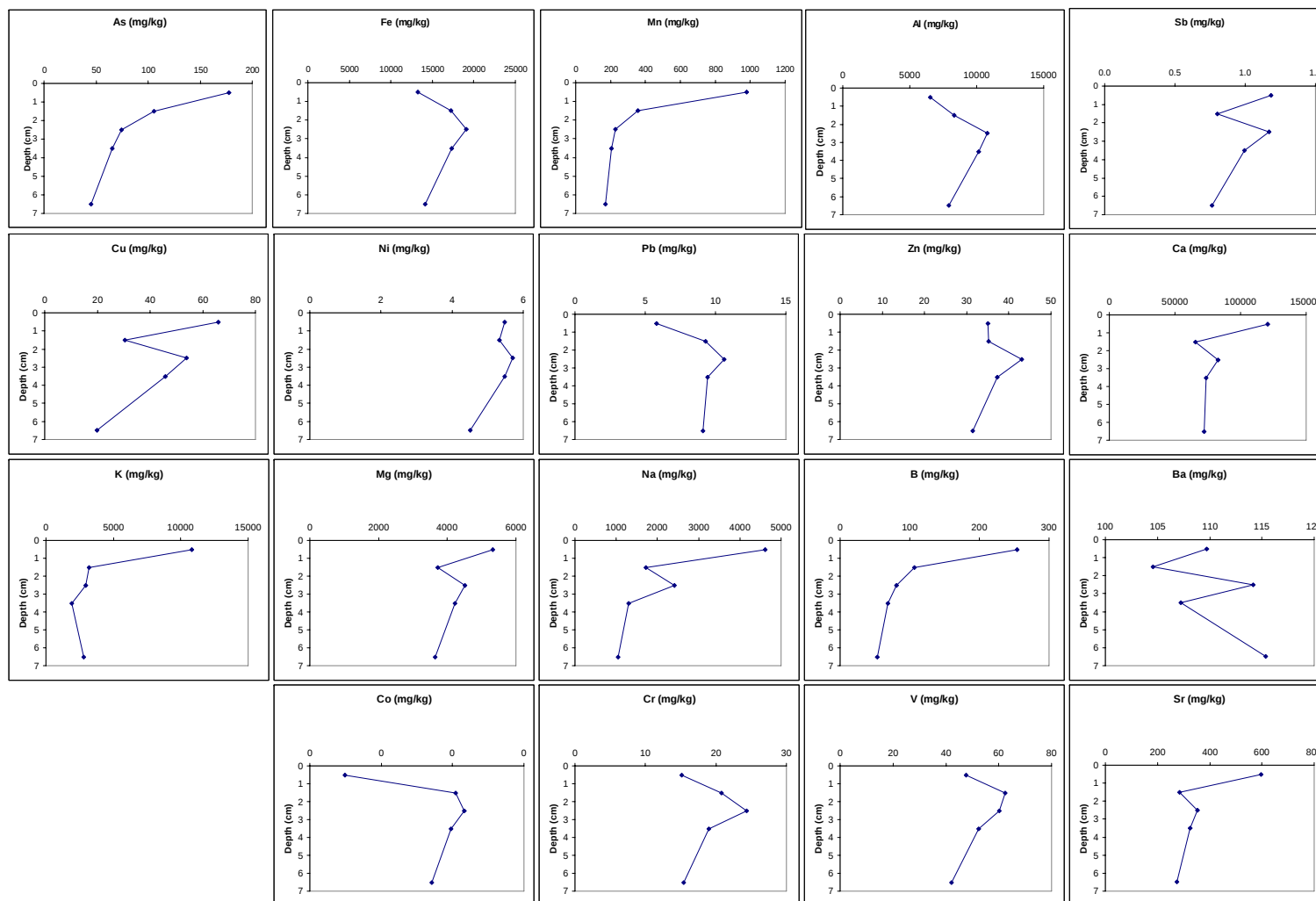
Loa at Lequena



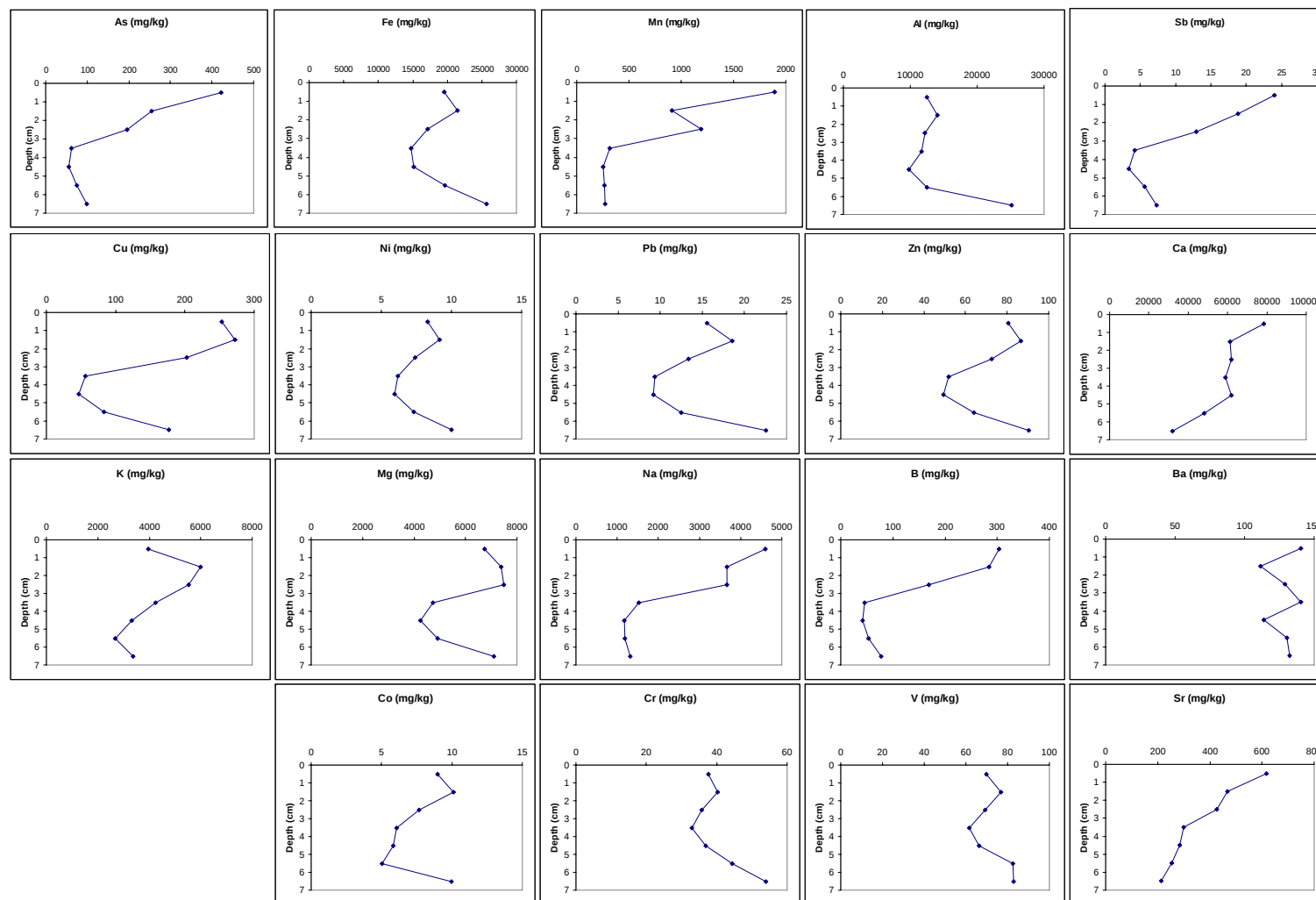
Loa at Conchi Reservoir



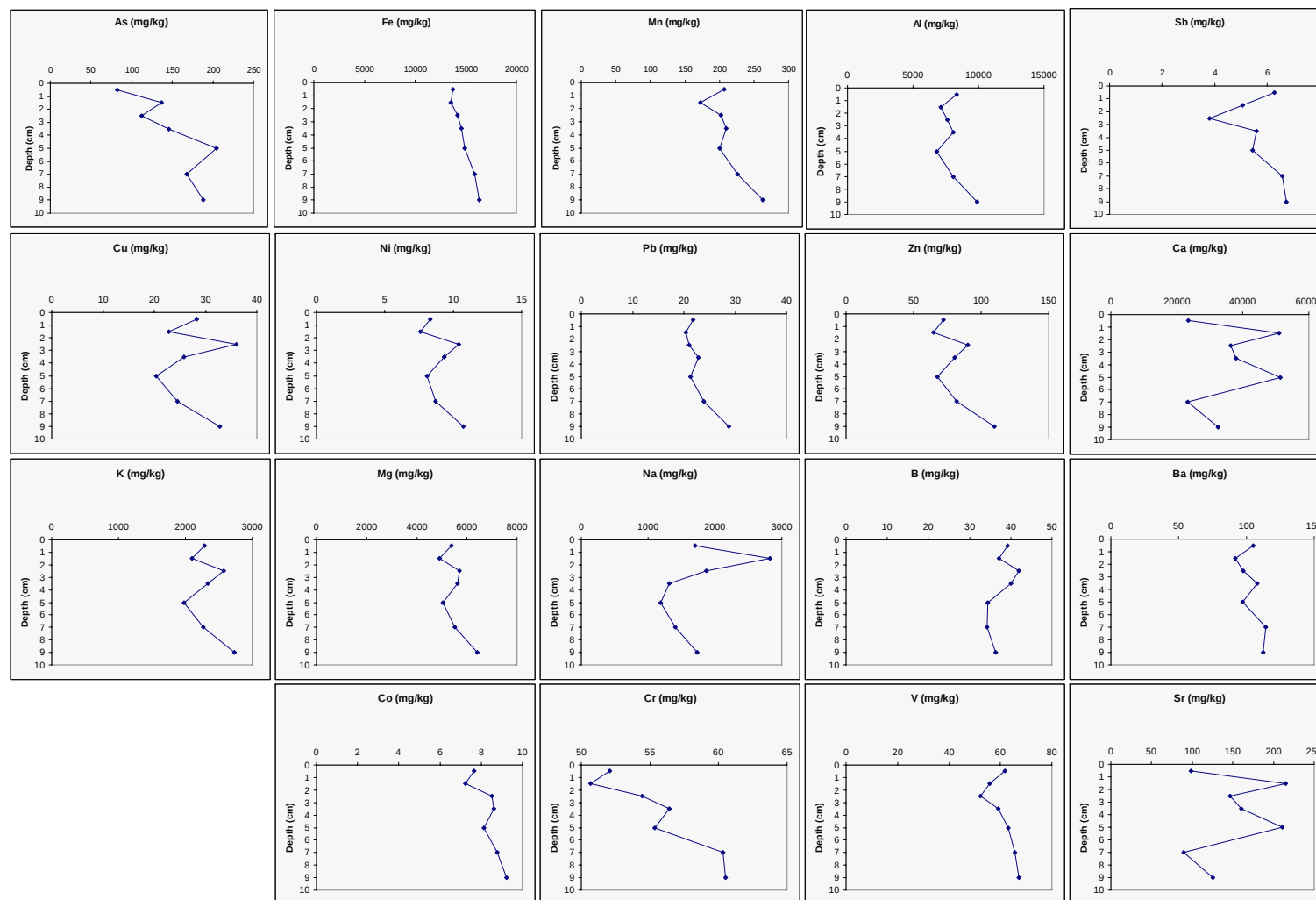
Loa before Salado junction



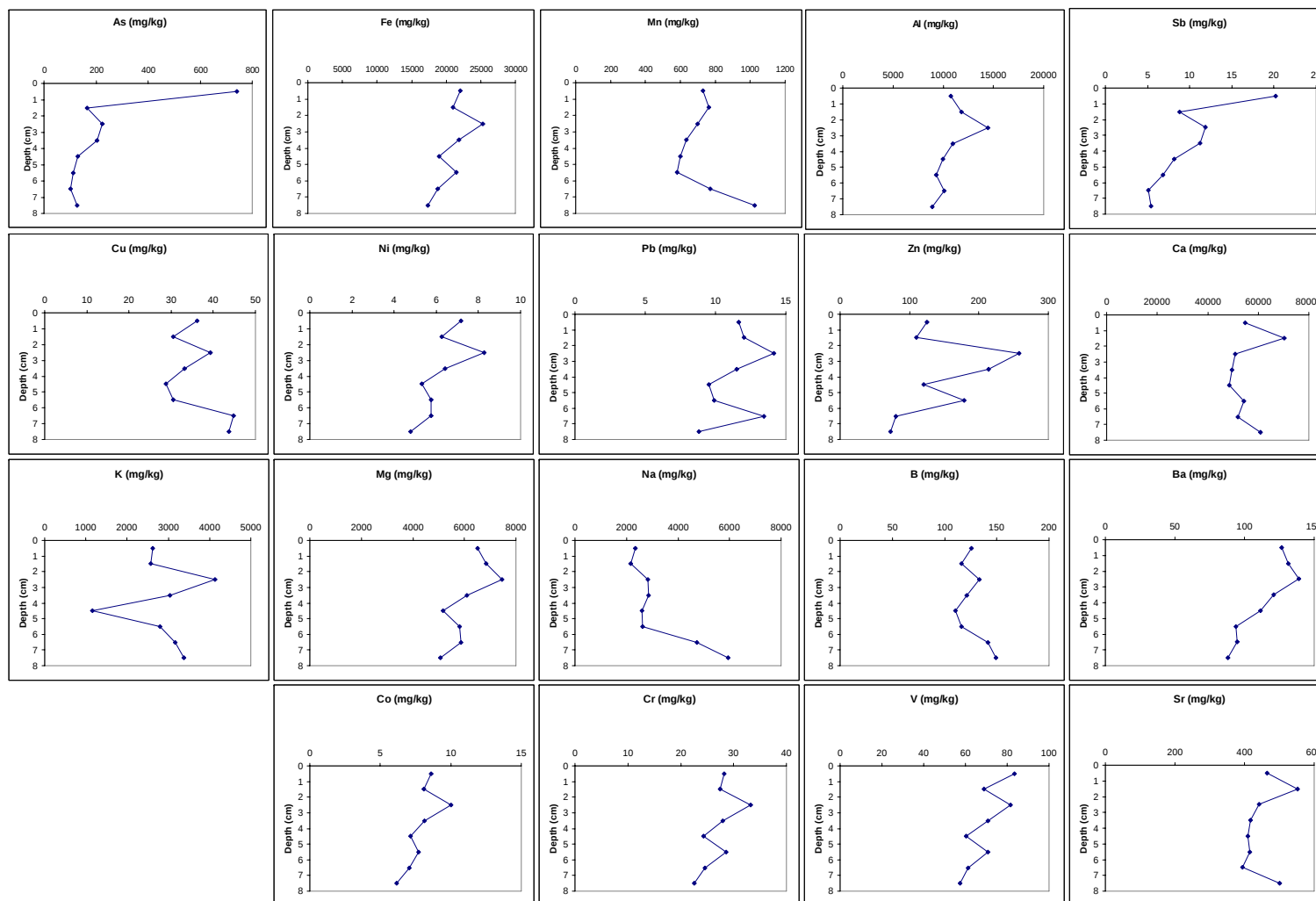
Loa after Salado junction



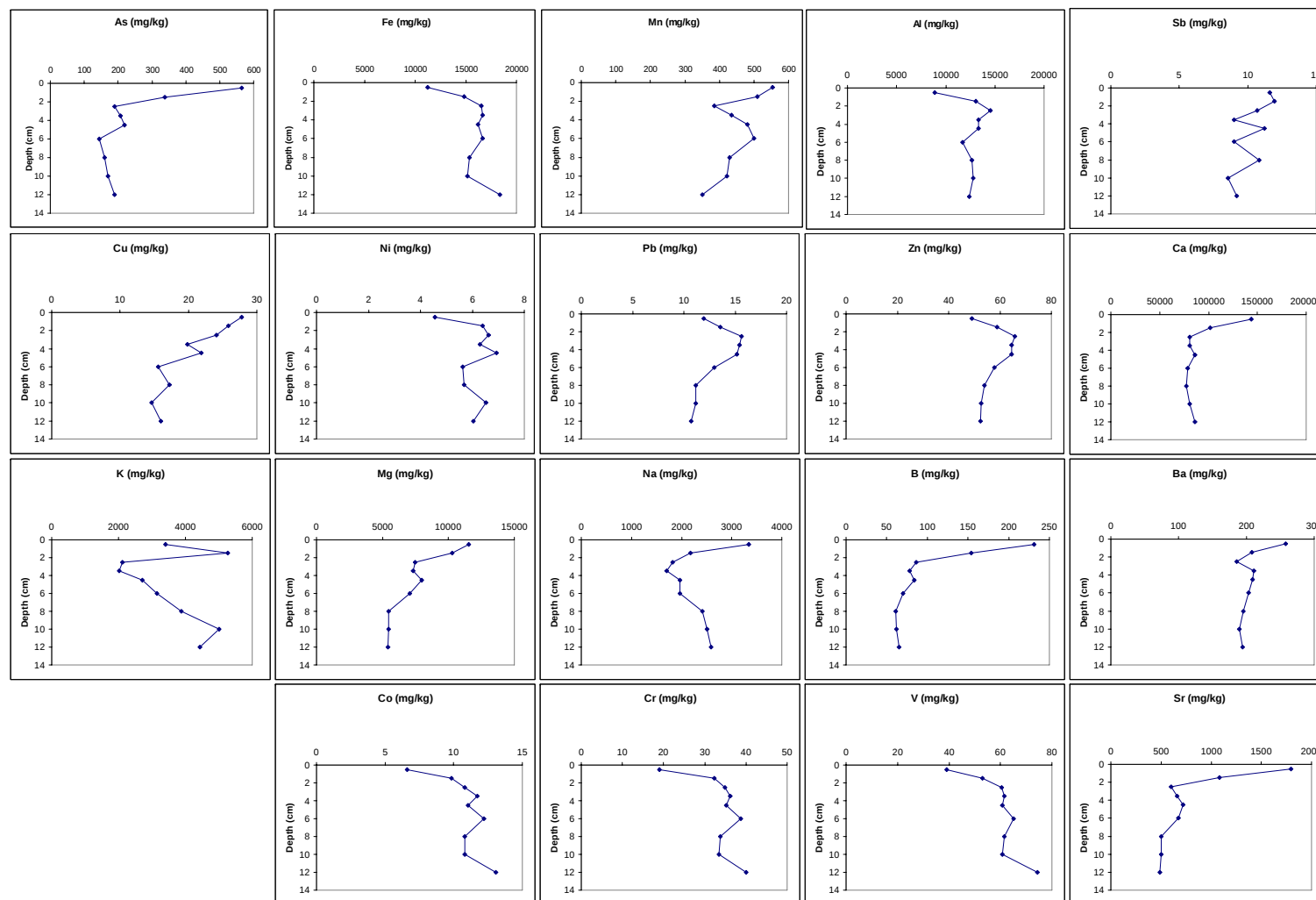
Loa at Angostura



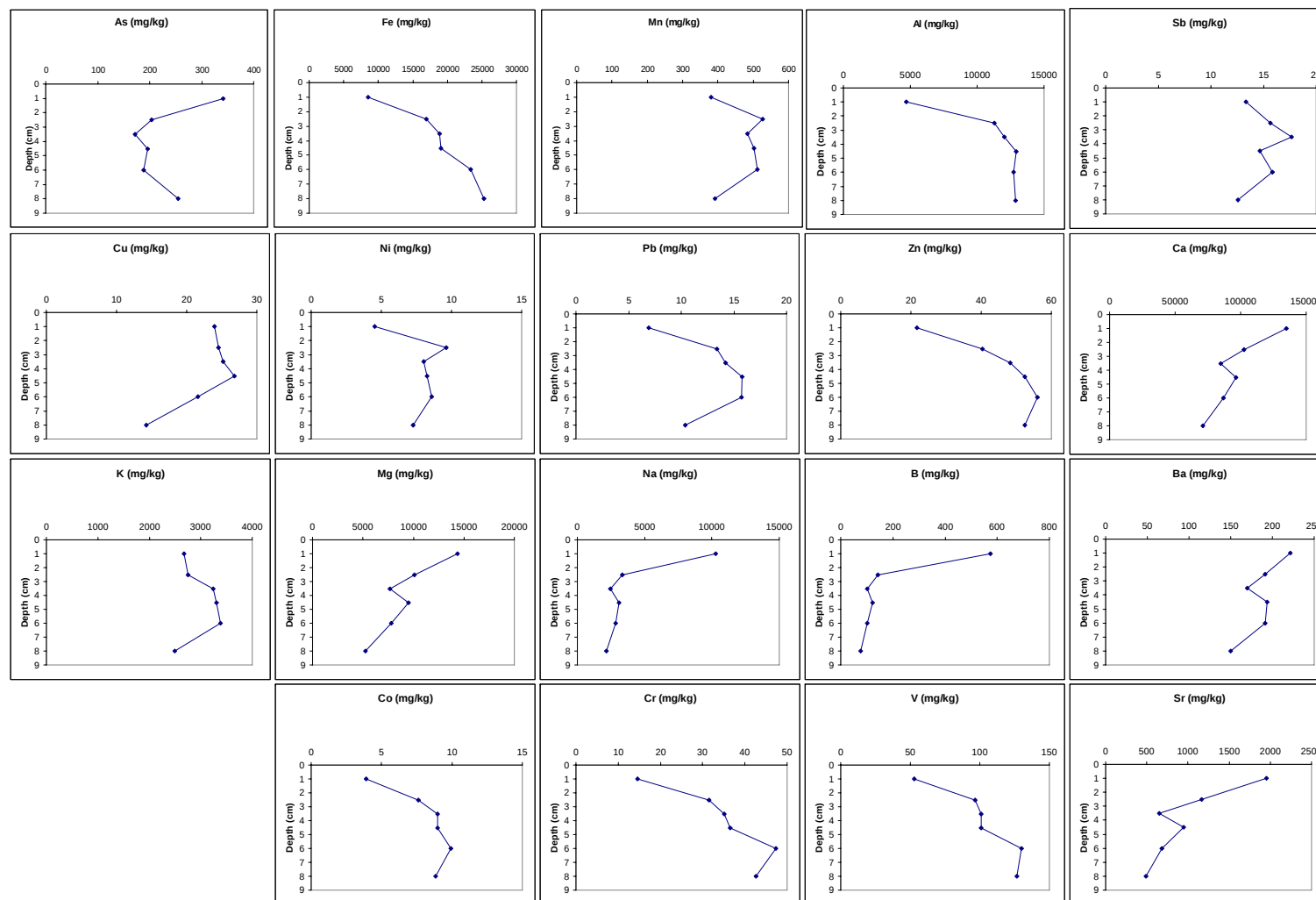
Loa at Yalquincha



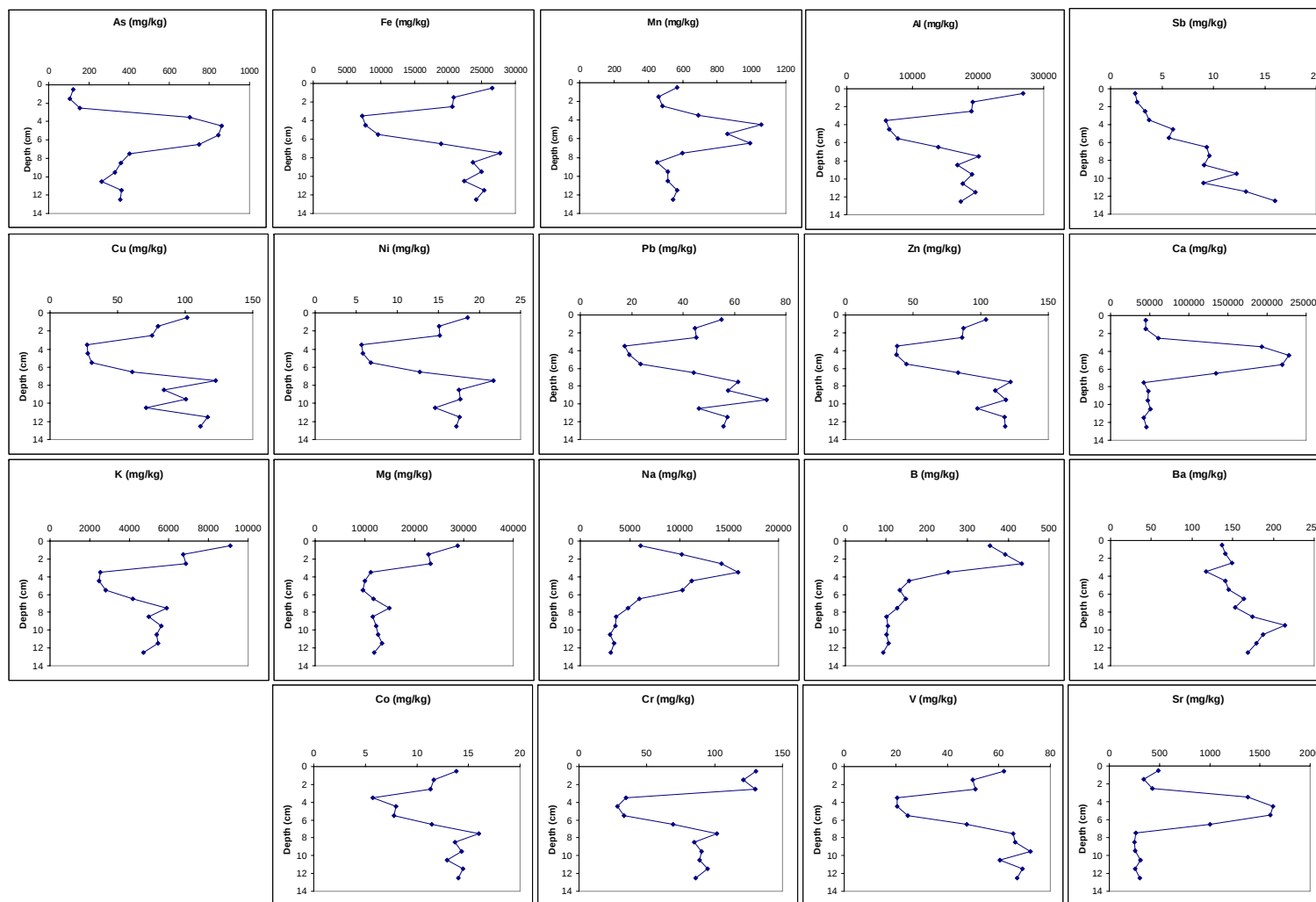
Loa at Cruce A



Loa at Cruce B



Loa at Sloman Reservoir

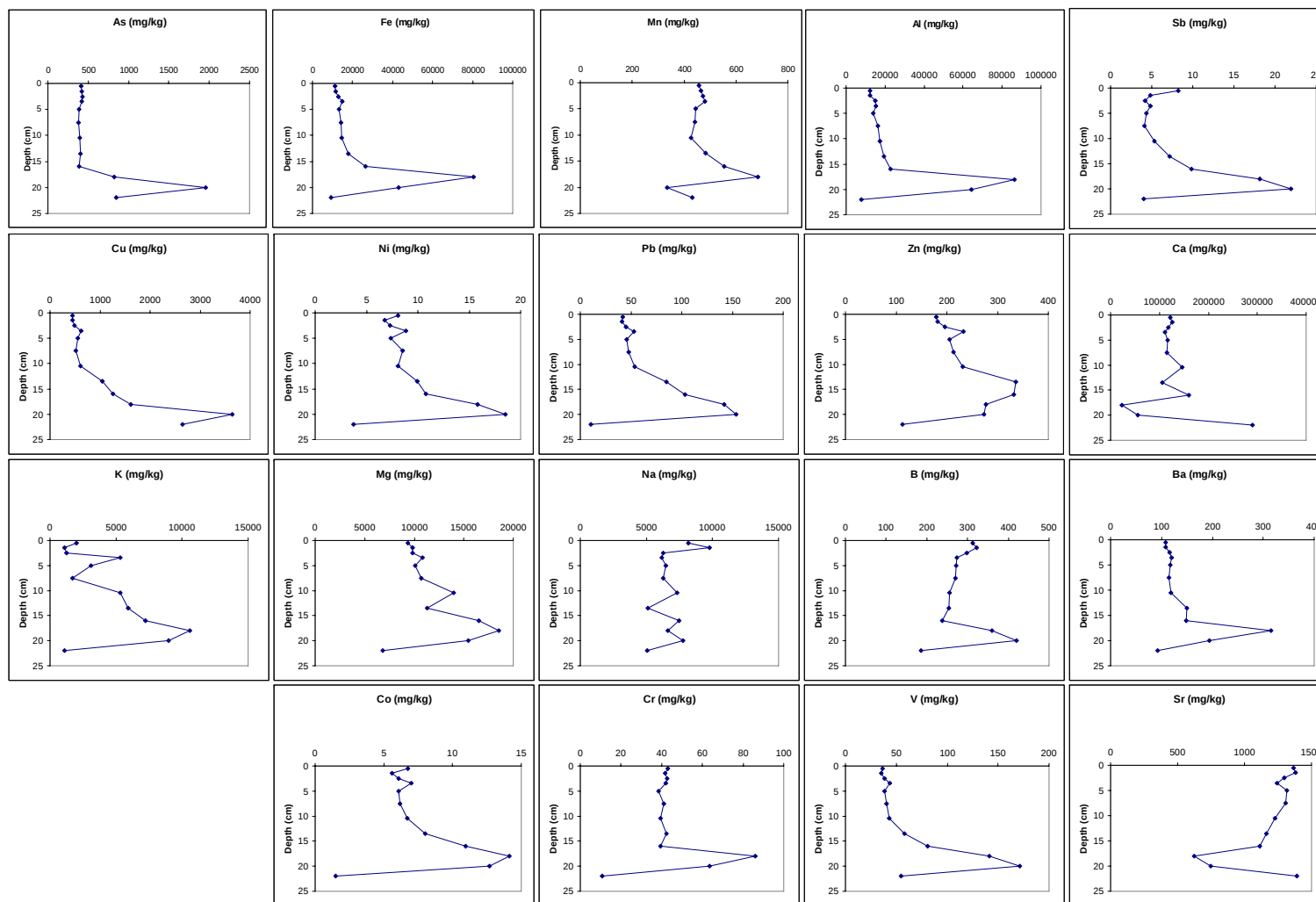


Loa at Quillagua

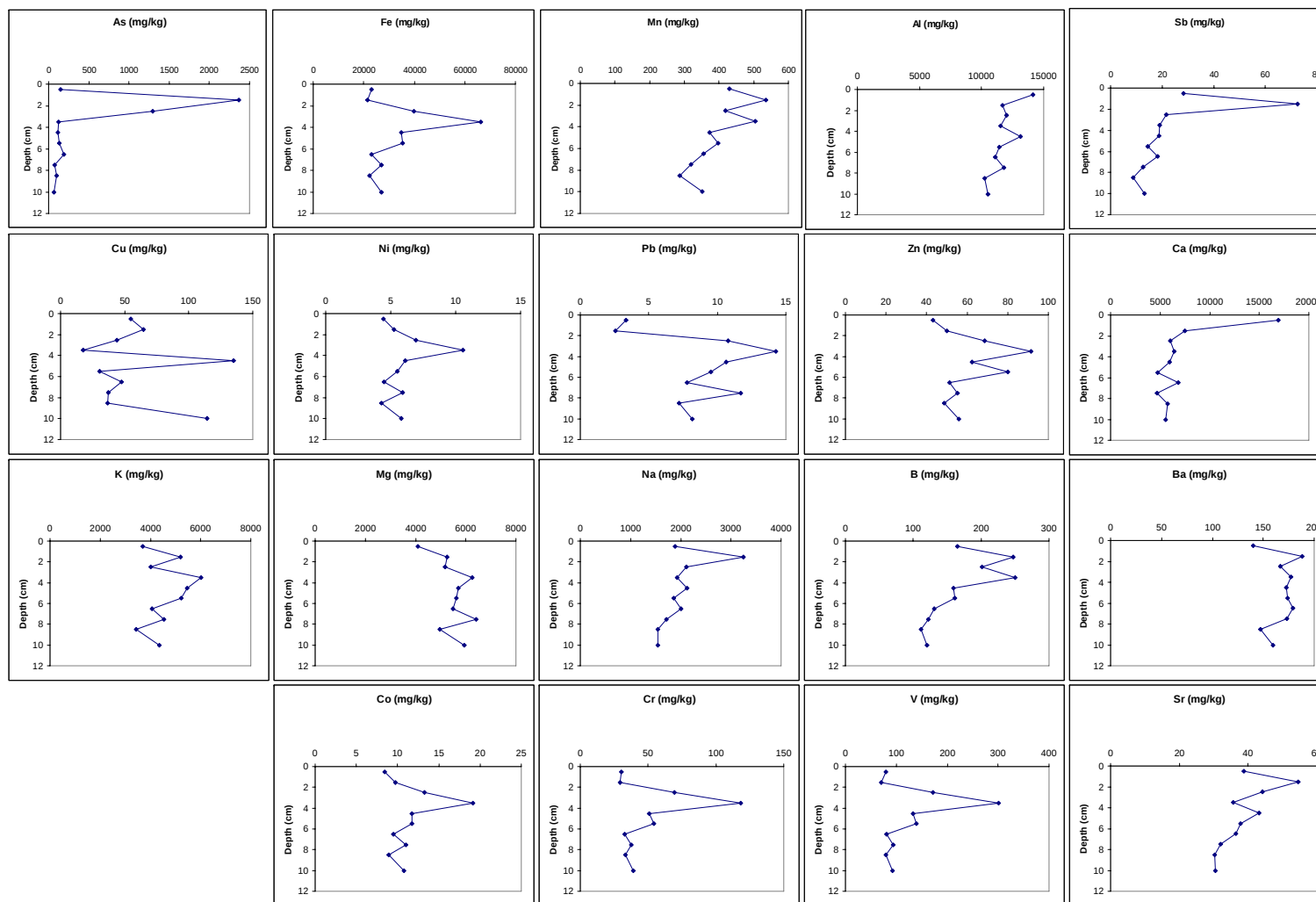
At this site only one data point is available (0-5 cm sediment section), therefore no profiles are presented. The following table reports the values for this point.

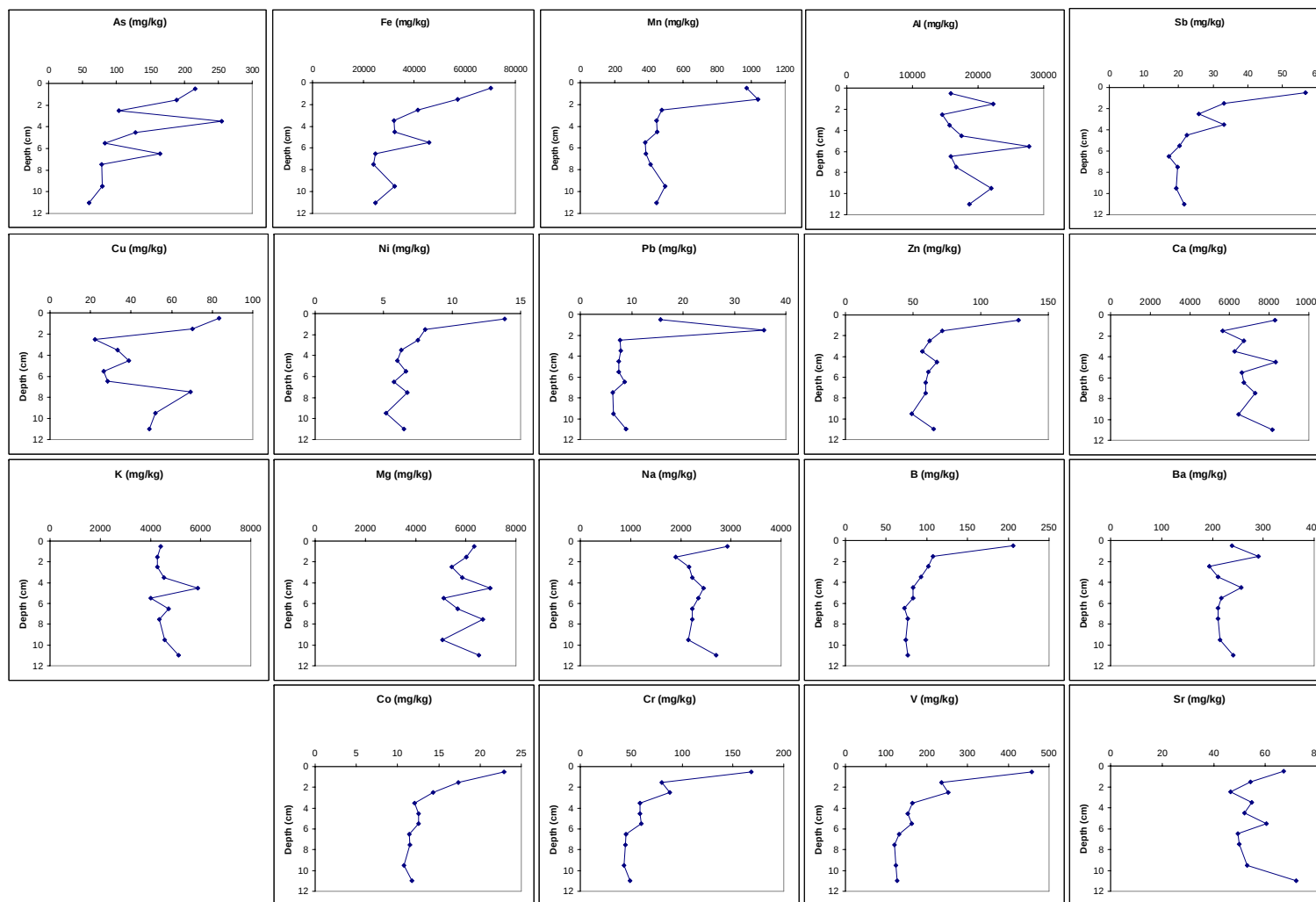
Element	Content in sediment (mg/kg)
As	770
Sb	4
Cu	61
Fe	33202
Mn	818
Ni	14
Pb	25
Zn	95
Ca	43588
K	6584
Mg	15752
Na	8418
Al	21868
B	331
Ba	141
Co	11
Cr	65
V	76
Sr	530

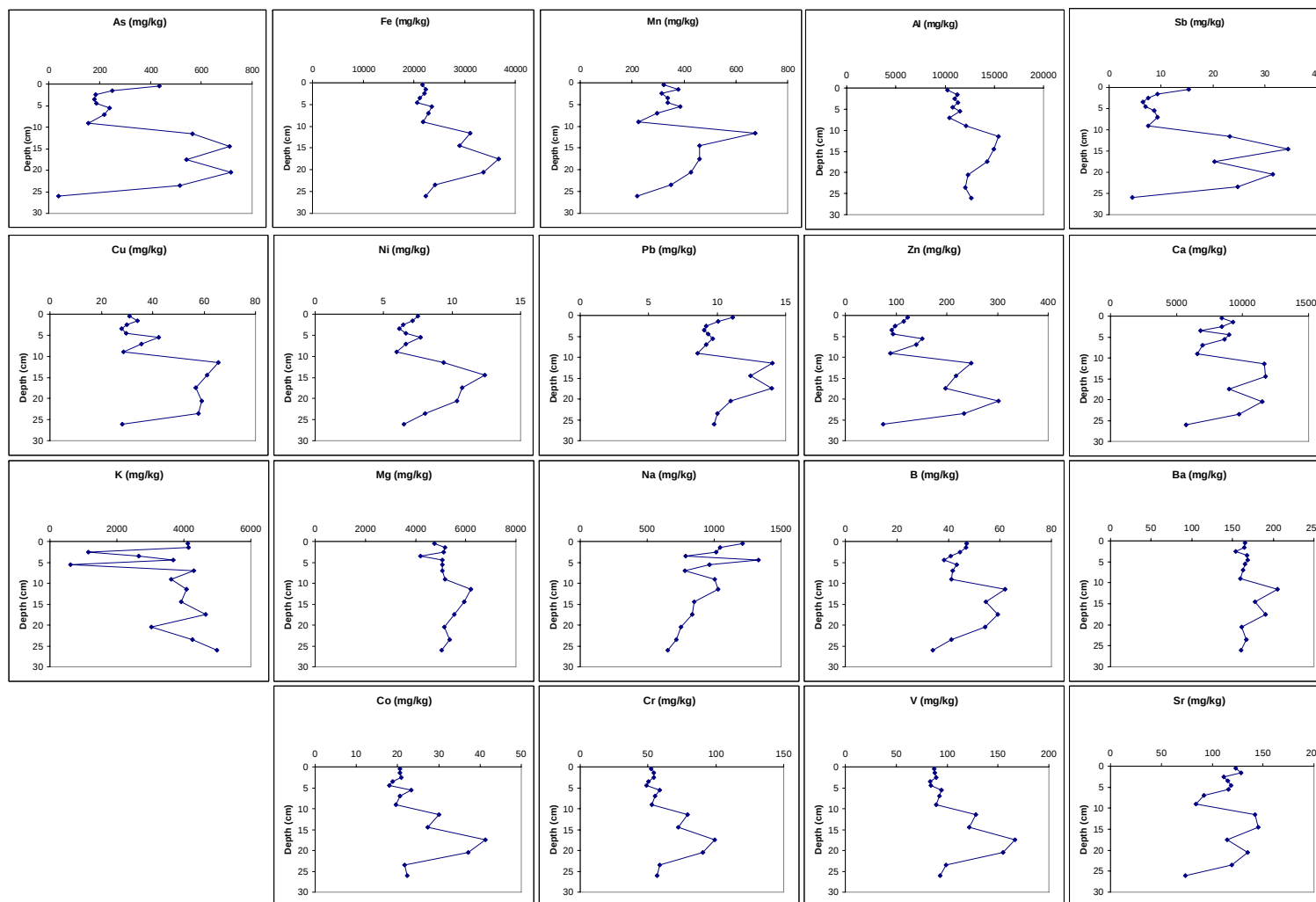
San Salvador Wetland



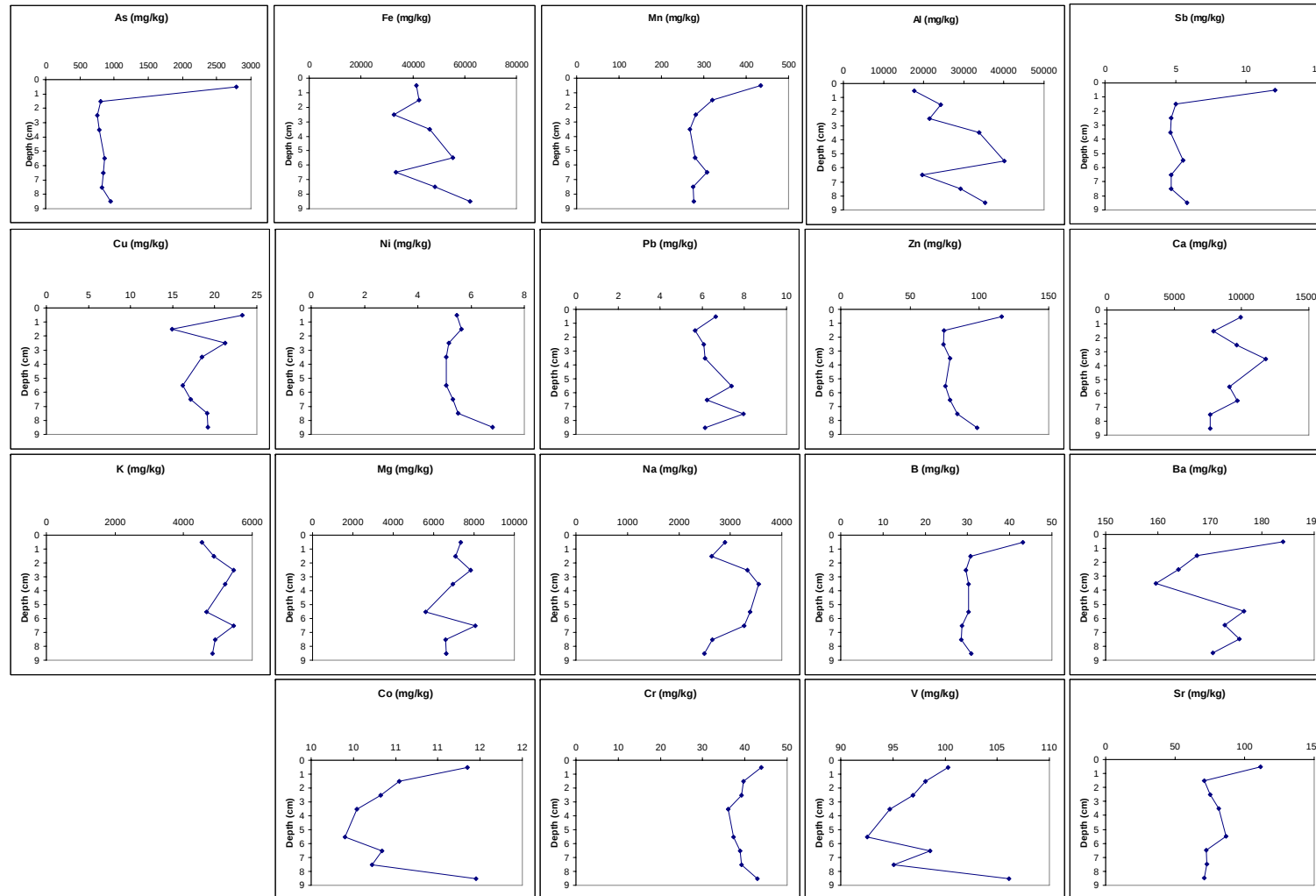
Salado at Codelco Reservoir A



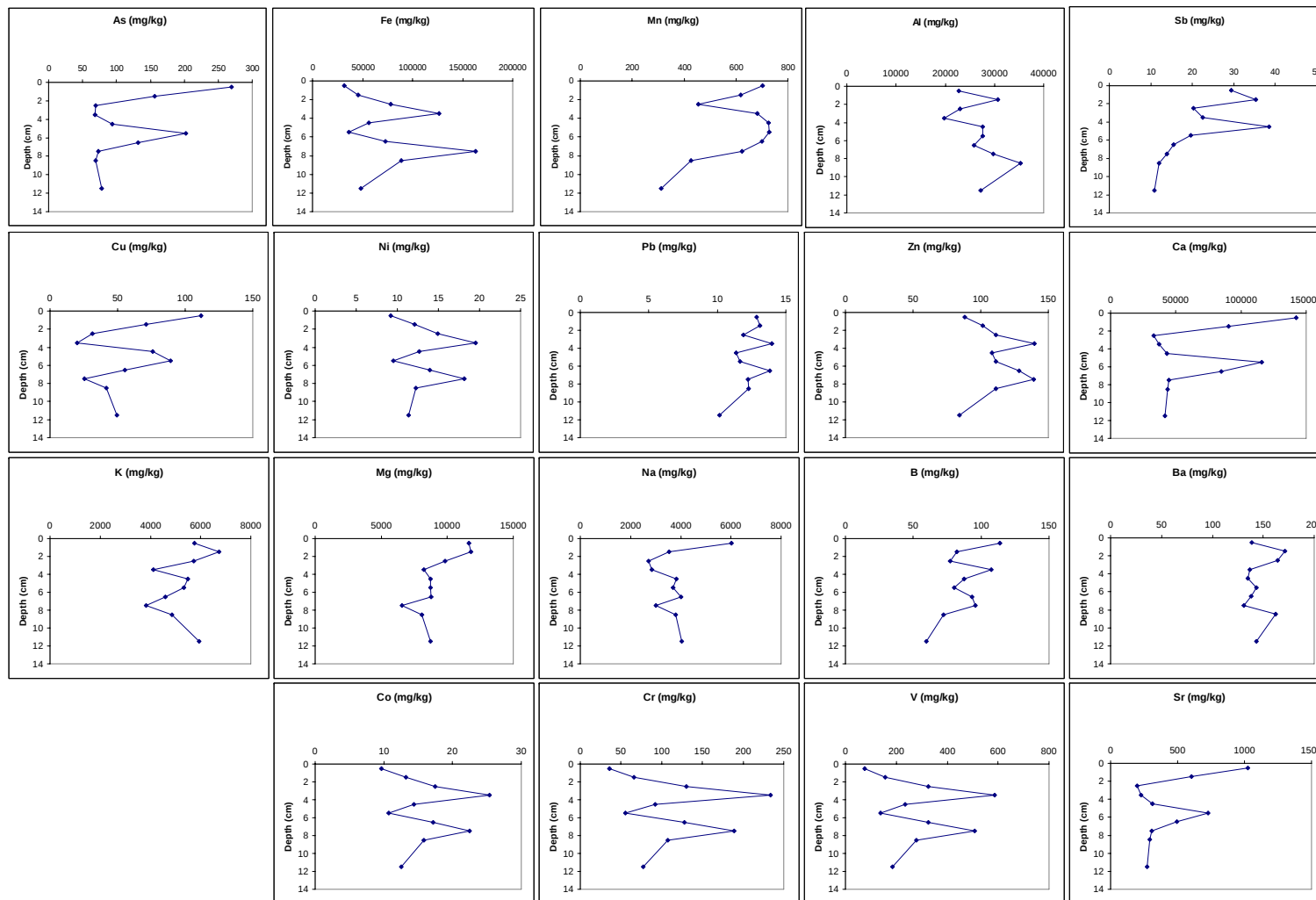
Salado at Codelco Reservoir B

Salado Ayquina A

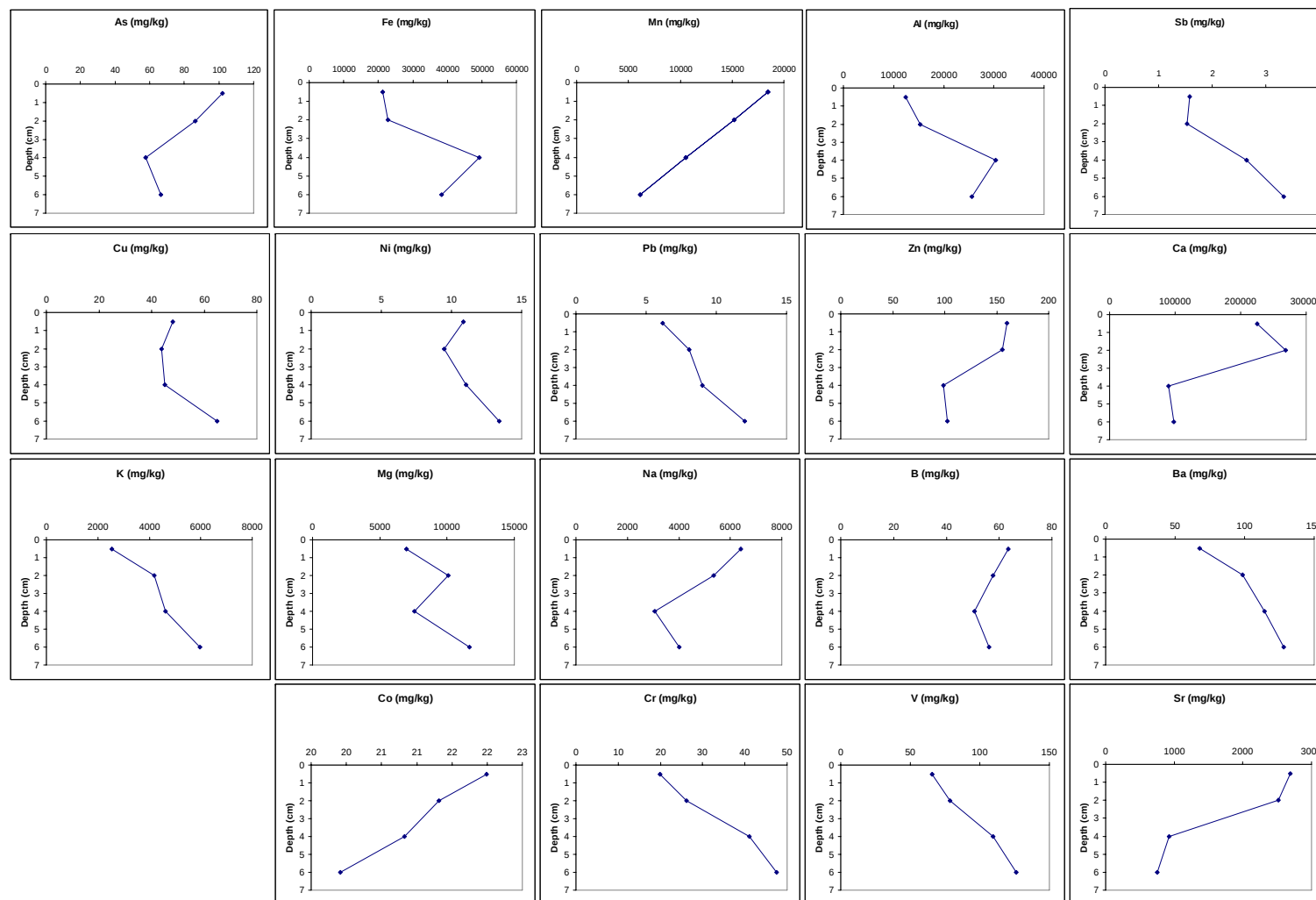
Salado Ayquina B



Salado at Baden



Salado Spring



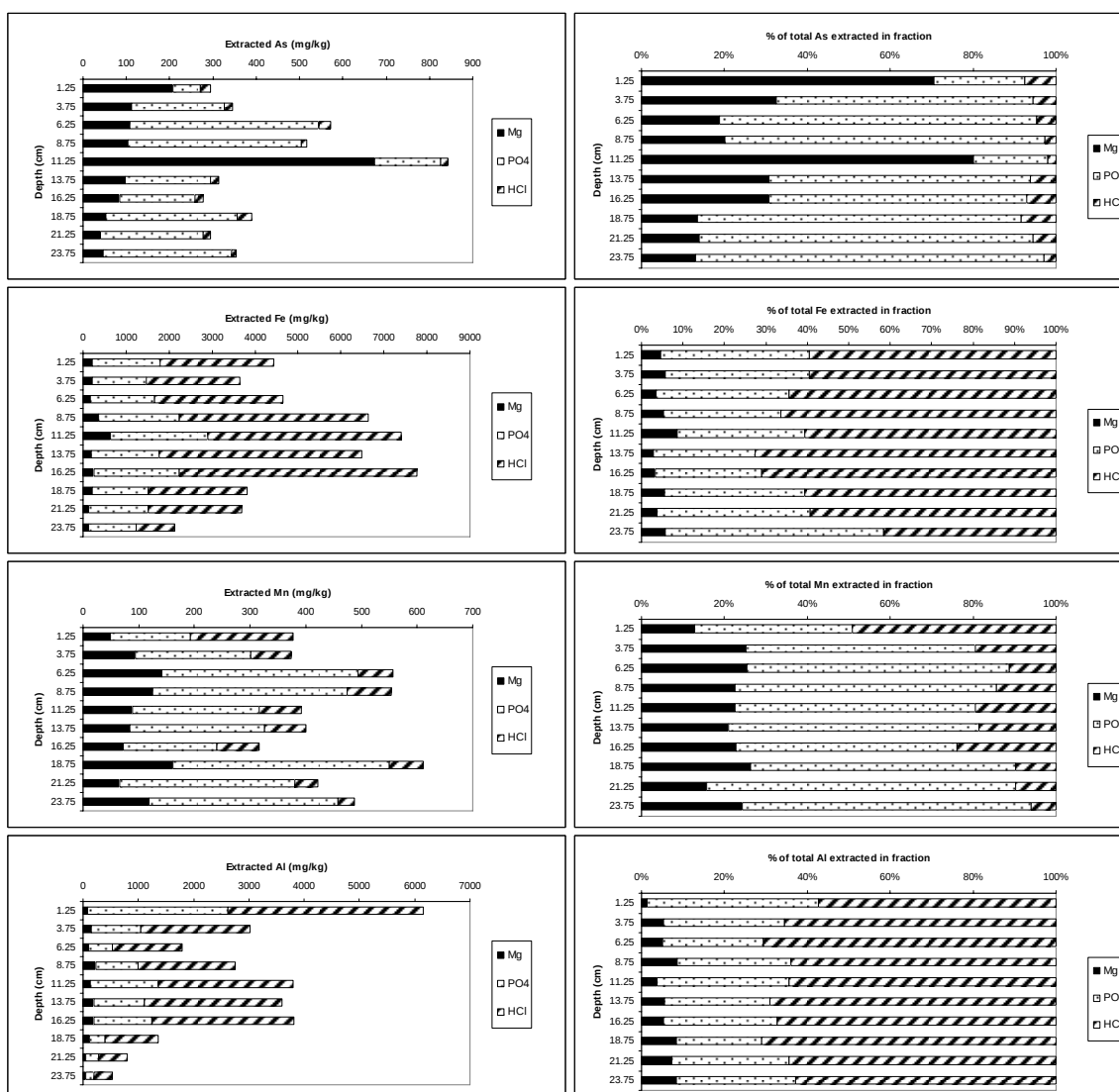
APPENDIX C: Elemental correlations with arsenic in sediment cores by site
(Pearson coefficient “R”)

Element	Site									
	Loa Lequena	Loa Conchi	Loa before	Salado	Salado	Salado	Salado	Salado	Salado	Loa after
			Salado	Codelco A	Codelco B	Spring	Ayquina A	Ayquina B	Baden	Salado
Sb	0.0	-0.4	0.5	0.9	0.7	-0.8	1.0	0.4	0.4	1.0
Cu	0.5	0.7	0.7	0.0	0.2	-0.3	0.9	0.2	0.9	0.8
Fe	0.0	-0.4	-0.4	-0.2	0.4	-1.0	0.8	-0.1	-0.6	0.2
Mn	0.9	0.6	1.0	0.6	0.5	0.9	0.7	0.4	0.5	1.0
Ni	-0.2	0.0	0.4	0.0	0.4	-0.5	0.9	0.1	-0.7	0.4
Pb	0.4	0.2	-0.8	-0.5	0.4	-0.8	0.7	0.1	0.2	0.3
Zn	0.4	-0.1	-0.1	-0.1	0.4	1.0	0.9	0.2	-0.4	0.6
Ca	0.0	0.9	0.8	0.0	-0.2	0.9	0.9	0.1	1.0	0.7
K	0.3	0.1	0.9	0.1	-0.1	-0.8	0.2	-0.2	0.4	0.4
Mg	0.2	0.5	0.8	-0.2	0.1	-0.3	0.6	0.1	0.7	0.6
Na	-0.5	0.2	0.9	0.9	0.0	1.0	-0.1	-0.2	0.8	0.9
Al	0.3	0.1	-0.6	0.0	-0.4	-1.0	0.6	-0.4	-0.2	-0.1
B	0.8	-0.1	1.0	0.6	0.5	0.9	0.8	0.7	0.4	1.0
Ba	0.7	0.7	-0.4	0.4	0.2	-0.9	0.5	0.3	-0.1	0.2
Co	-0.4	-0.3	-0.8	-0.1	0.5	0.8	0.7	0.2	-0.7	0.6
Cr	-0.3	-0.7	-0.3	-0.1	0.5	-0.9	0.7	0.3	-0.7	-0.2
V	-0.4	-0.5	0.0	-0.1	0.5	-0.9	0.8	0.1	-0.7	0.0
Sr	0.3	0.7	0.9	0.9	0.0	0.9	0.8	0.6	1.0	1.0

Element	Site						Average correlation for individual cores	Number of cores with correlation > 0.7	Number of cores with correlation < -0.7	Tendency (positive or negative correlation)
	Loa Angostura	Loa Yalquincha	Loa Cruce A	Loa Cruce B	Loa Sloman	San Salvador Wetland				
Sb	0.3	0.9	0.6	-0.8	0.0	0.8	0.3	6	2	+
Cu	-0.4	0.0	0.8	-0.2	-0.7	0.9	0.3	7	1	+
Fe	0.7	0.4	-0.8	-0.7	-0.8	0.5	-0.1	2	4	-
Mn	0.4	0.0	0.7	-0.9	0.9	-0.3	0.5	7	1	+
Ni	0.1	0.5	-0.6	-0.9	-0.8	0.7	0.0	2	3	-
Pb	0.4	0.2	-0.1	-0.9	-0.7	0.6	0.0	1	4	-
Zn	0.2	0.0	-0.4	-0.8	-0.7	0.1	0.1	2	2	-
Ca	0.4	0.0	1.0	0.5	0.9	-0.2	0.4	7	0	+
K	-0.1	0.0	0.1	-0.8	-0.9	0.5	0.0	1	3	-
Mg	0.1	0.3	0.9	0.5	-0.7	0.3	0.3	2	1	-
Na	-0.4	-0.4	0.7	0.9	0.3	0.1	0.3	7	0	+
Al	0.0	0.2	-0.7	-0.9	-0.9	0.6	-0.2	0	4	-
B	-0.7	0.0	1.0	0.9	-0.4	0.6	0.5	8	1	+
Ba	0.2	0.4	0.9	0.4	-0.3	0.4	0.2	3	1	+
Co	0.5	0.4	-0.9	-0.9	-0.7	0.4	0.0	2	5	-
Cr	0.6	0.3	-0.9	-0.7	-0.9	0.4	-0.2	1	6	-
V	0.6	0.7	-0.9	-0.7	-0.7	0.8	-0.1	3	5	-
Sr	0.3	0.2	1.0	0.7	0.9	-0.6	0.6	10	0	+

APPENDIX D: Sequential extraction procedure results

As, Fe, Mn, and Al extracted by each step for a sediment core from the Sloman Reservoir (Core C). Graphs on the left show total content extracted by the three steps of the procedure (expressed as mg/kg wet basis). Graphs on the right show element extraction as a percentage of the total extracted in the three steps.



APPENDIX E: X-Ray Diffraction results

Diffraction patterns for the sediment samples from Ayquina, Quillagua and Sloman.

