



Differential arsenic binding in the sediments of two sites in Chile's lower Loa River basin



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HIGHLIGHTS

- Contrasting As enrichment in fluvial sediments was found for two neighboring sites.
- Vegetation and sediment OM were also contrasting for the two river reaches.
- A strong association between As, Mn and OM was found in the vegetated site.
- A strong association between As, Ca and Sr was found in the poorly vegetated site.
- As immobilization in sediments in a fluvial reach may be enhanced by vegetation.

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ABSTRACT

Fluvial sediments from two lower Loa River basin sites in northern Chile were compared in order to probe the effects of vegetation and organic matter (OM) on As accumulation in fluvial environments. The two sites were the Sloman dam, which lacks macrophytes and has a low OM content (2.4%) in sediments, and the Quillagua Oasis, which is 23 km downstream from the Sloman site and has a higher OM (6.2%) in sediments and abundant aquatic plant life. The Quillagua site had preferential As enrichment with a co-occurrence pattern that differed from that of the Sloman site, which had a lower As concentration (1528 vs. 262 mg/kg d.w., respectively). At the Quillagua site, As concentration was strongly correlated with Mn and OM ($r = 0.91$ and 0.85 , respectively); while at the Sloman site, As concentration in sediments was significantly correlated with Ca and Sr ($r = 0.63$ and 0.54 , respectively). Sequential extraction analyses showed that the Sloman site had higher percentage of easily exchangeable As within the surface sediment (12%, 45 mg/kg d.w.) compared with the Quillagua site (3%, 40 mg/kg d.w.). These contrasting results suggest that both vegetation and OM control the immobilization and accumulation of As in the arid Loa River basin.

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1. Introduction

Arsenic (As) from natural and anthropogenic sources can be found in soils and aquatic environments. The As is a toxic metalloid that limits the activities of most living organisms in aquatic systems. Moreover, it has been estimated that more than 100 million people are exposed to health risks from unsafe As concentrations in drinking water in countries like India, Bangladesh, Argentina, Chile, China, Mexico, Mongolia, Germany, and the United States (Bhattacharya et al., 2007; Hossain, 2006).

Previous research has focused on the occurrence of As in subsurface environments due to a larger population exposed to high levels of

this element in groundwater in Southeast Asia. Comparatively, little attention has been given to the factors controlling the dynamics of As in rivers. To further improve the knowledge of the behavior of As in aquatic environments it is necessary to understand the factors and processes that control its mobility in rivers. This understanding is critical for rivers located in arid regions where water sources are scarce and evaporation processes increase the aqueous concentrations of toxic metals and metalloids originated from natural and anthropogenic sources. Furthermore, arid conditions highlight the role of fluvial sediments as potential repositories of As, scavenging or releasing this toxic element depending on biogeochemical factors.

Arsenic sorption and desorption into inorganic and organic phases within sediments are the key processes that control its mobility and concentration in rivers. Among the inorganic phases associated with As in aquatic environments, hydrous ferric oxides (HFO) and manganese oxides are the most prominent and frequently studied sorbents (Deschamps et al., 2003; Li et al., 2009; Raven et al., 1998).

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Among the organic components, As has been associated with plants, microorganisms, or directly with organic matter (OM) (Bhattacharya et al., 2007).

Previous research has shown that plants can control As bioavailability with two main strategies: i) sorbing aqueous As onto Fe oxides coating the surfaces of their roots, thus creating a shielding effect (Blute et al., 2004; Hansel et al., 2002; Hu et al., 2005) and ii) incorporating As and later metabolizing or storing it in different tissues (Aldrich et al., 2007; Favas et al., 2012; Ma et al., 2001; Meharg and Macnair, 1991; Meharg and Whitaker, 2002; Zhao et al., 2009).

The OM in natural waters and sediments may also control As mobility. For example, OM can modulate the complexation of As with hematite, goethite or ferrihydrite by promoting its desorption and increasing its mobility (Bauer and Blodau, 2006; Buschmann et al., 2006; Redman et al., 2002; Wang and Mulligan, 2006). Studies in sediments with high As content have found a strong correlation between As content and OM (Anawar et al., 2003; Meharg et al., 2006; Wang et al., 2010), with biological activity being a strong mediator for its mobilization from sediments (Guo et al., 2008).

The extent of As association to minerals and OM can also be controlled by the environmental geochemical conditions, such as pH, redox potential or the presence of other minerals and ions (Cheng et al., 2009; Masscheleyn et al., 1991). The pH plays an important role in determining the speciation of inorganic or organic components in water that may serve as either sorbents or desorbents. For inorganic phases such as metals exposed to oxidizing conditions at $\text{pH} < 7$, As is immobilized by co-precipitation/sorption with Fe and Mn oxy-hydroxides. Conversely, when Fe and Mn oxy-hydroxides are exposed to basic environments, As desorption is favored (Smedley and Kinniburgh, 2002). Under acidic sulfate reducing conditions As can be accumulated as stable sulfur minerals (Harvey et al., 2002; Masscheleyn et al., 1991; O'Day et al., 2004). Biological components such as macrophytes can induce oxygenated micro-environments around their roots in surface sediments, inducing favorable conditions for the formation of Fe oxides (Foster et al., 2011; Gault et al., 2011; Harrington et al., 1998). The extent of the association of As with different solid phases is regulated by the ionic composition of the solution. For example, it has been shown that a Ca/As molar ratio > 1 and low dissolved Fe and Mn concentrations favor the association of As with calcite or kaolinite minerals (Di Benedetto et al., 2006; Moon et al., 2004). Similarly, silicates can control the potential of As co-precipitation with iron oxy-hydroxides (Ruiping et al., 2007). Thus, previous work in laboratory and natural environments has shown that a suite of biogeochemical processes control the mobility of As in fluvial environments. Within this body of knowledge, processes governing As mobility in arid fluvial environments have received less attention.

The purpose of this work is to investigate the role of vegetation and OM as influential factors for the enrichment and distribution of As in the lower Loa River basin sediments. The experimental design was based on the sediment sampling and analyses of two close sites with similar climatic conditions, where changes in the water chemistry due to contributions along the riverbed are marginal, but with contrasting vegetation and OM contents. These natural conditions are ideal for the comparative in situ study of the effects of abiotic and biotic factors on the As enrichment and mobility in fluvial systems.

2. Study area

The Loa River in northern Chile (Fig. 1) crosses the Atacama Desert from the east to the west and its main tributaries provide water for domestic, industrial and irrigation uses in this arid region. The water withdrawal along the river is $\sim 3.4 \text{ m}^3/\text{s}$, including irrigation of $\sim 1000 \text{ ha}$ of agriculture in the valley of the Loa and Salado rivers (Aravena and Suzuki, 1990). Besides agriculture, mining (e.g., the Chuquicamata copper mine) and the chemical industry (saltpeter industry) are relevant users. The estimated water use is: 1.77 and $0.24 \text{ m}^3/\text{s}$,

respectively (Mondaca et al., 1994), causing the river flow to be lower than $1 \text{ m}^3/\text{s}$ in sections with high water extraction rate. Therefore, the Loa River is a critical water resource in a water-scarce region with an intense water usage pattern.

The flow of water in the Loa River usually shows seasonal variations in the range of $0.5\text{--}3 \text{ m}^3/\text{s}$ (GARHIN, 1994). During heavy-rain events occurring during the Altiplano Winter (storm events concentrating annual rainfall between December through March, also known as Bolivian Winter), the flow of the Loa River may exceptionally increase up to four orders of magnitude. Recent important storm events occurred in March 1997, and February of 2000, 2001, 2011 and 2012 and have been attributed to the El Niño Southern Oscillation (ENSO) climatic phenomenon. Due to geomorphological and hydrological conditions along the riverbed, high sediment transport events may be observed from high-flow high-velocity events.

Along the Loa watershed, three sections with distinct chemical properties can be defined: Upper, Middle and Lower Loa. The upper Loa comprises the zone between the origin of the river (at the foot of the Miño Volcano) and the confluence with the Salado River, near the Chiu-Chiu village (Fig. 1). The Upper Loa has an average flow of $1.2 \text{ m}^3/\text{s}$, $\text{pH} = 7.7$, electrical conductivity (EC) = 2.8 mS/cm and a total As concentration of 0.2 mg/L . The Middle Loa comprises the zone between the confluence Loa–Salado River near the Chiu-Chiu village and the confluence of Loa–San Salvador River in the Chacance village, with an average flow of $0.25 \text{ m}^3/\text{s}$, $\text{pH} = 7.9$, $\text{EC} = 8.2 \text{ mS/cm}$ and a As concentration of 1.4 mg/L . Finally, the Lower Loa comprises the zone between the Chacance village and the discharge of the Loa River to the Pacific Ocean, with an average flow of $0.44 \text{ m}^3/\text{s}$, $\text{pH} = 8.0$, $\text{EC} = 14.1 \text{ mS/cm}$ and a As concentration of 2.2 mg/L (Hamamé, 2002; Romero et al., 2003). The presence of As in the Middle Loa is attributed to natural sources, notably the contribution from El Tatio Geothermal field to the Salado River ($0.7 \text{ m}^3/\text{s}$, $\text{As} = 21 \text{ mg/L}$) at the end of the Upper Loa, causing an average As concentration of 1.4 mg/L (Hamamé, 2002; Romero et al., 2003).

The As concentration in waters along the Middle and Lower Loa sections remain high due to several factors. Extreme desert climate favors high evaporation rates, high salinity, and the lack of surface tributaries and fresh groundwater contributions impedes dilution, while the neutral to alkaline pH of water hinders the sorption of As onto solid phases. The contribution of As to the Loa River from mining activities and wastes has not been discarded (Romero et al., 2003). The hydromorphology of the Lower Loa has been altered significantly since the early 1900s due to the construction of three dams: Sloman, Santa Fe and Santa Teresa (Fig. 1), altering the natural sediment flux from the Andes to the Pacific Ocean. Arroyo et al. (1999) reported that in February 1997, a temporary increase of the concentration of As and OM in sediments upstream from the Sloman dam was detected. Consequently, hydrological factors may play a significant role in the distribution of sediment repositories.

The Lower Loa River shows heterogeneity in vegetation coverage along the streambed, possibly linked to local geomorphological factors. Abundant vegetation is found in some reaches, while in other places, plants do not grow, particularly in reservoirs. This heterogeneity offers a unique opportunity to investigate how biotic and abiotic factors modulate the association and accumulation of As in sediments in different sections of the river.

The Quillagua oasis and the Sloman dam are two sites, located in the Lower Loa River (Fig. 1). While the Quillagua oasis is a natural wetland with abundant aquatic life (cattail), where *Scirpus americanus* (Becerra and Faúndez, 2001; Sancha and Castro, 2001) nearly covers the river bed and banks, the Sloman dam is a reservoir 23 km upstream from the Quillagua oasis lacking completely of macrophytes. The Sloman dam was built between 1905 and 1911 to provide hydroelectricity to saltpeter mines.

The absence of macrophytes in the Sloman dam may be attributed to two factors: (i) the colonization of plants is constrained by the

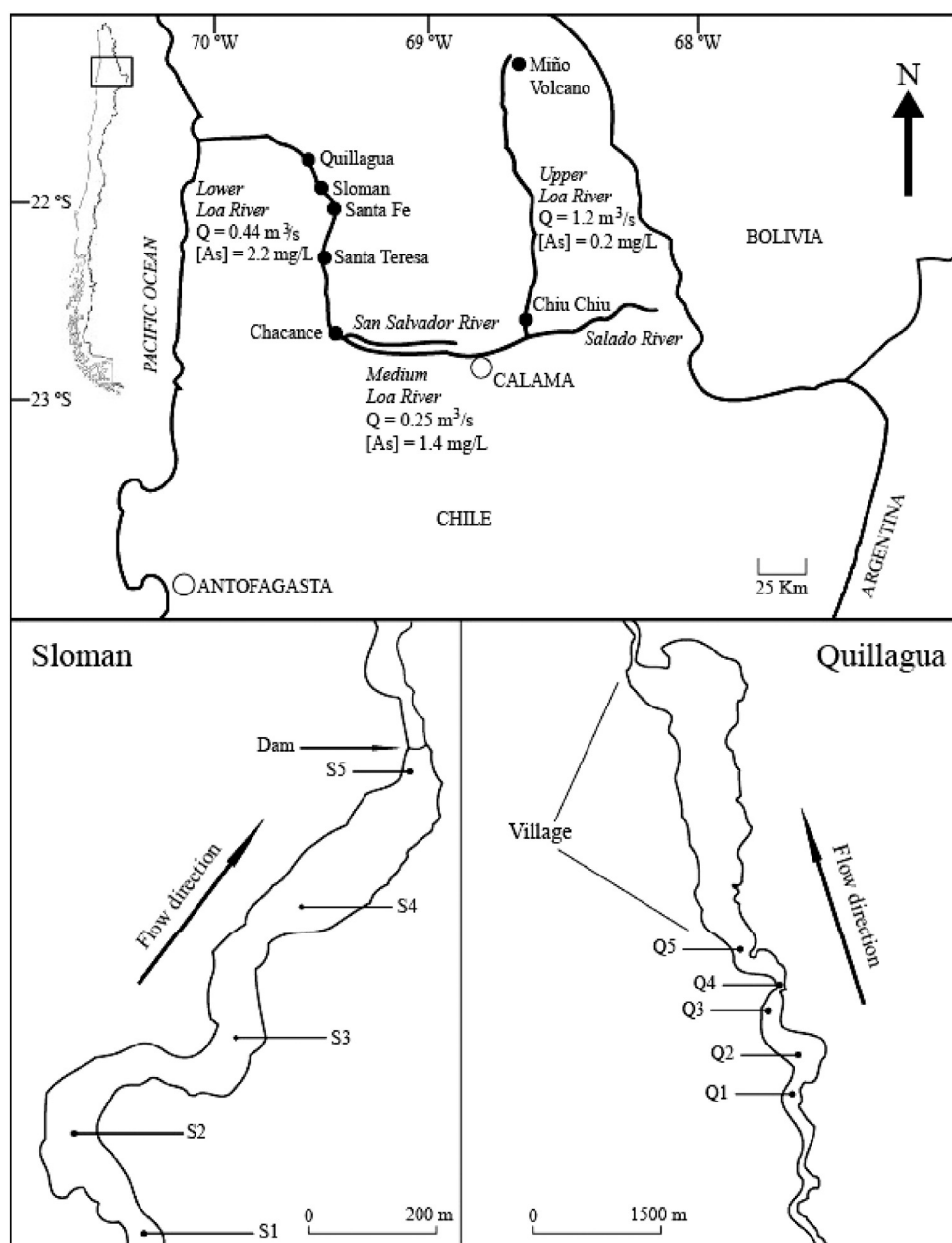


Fig. 1. The Loa River basin, northern Chile, Sloman and the Quillagua study sites. The point S1 to S5 and Q1 to Q5 correspond to collection of sediments cores, plants (only for Quillagua). Samples of water column for Sloman and Quillagua were done in S5 and Q3 respectively.

water depth and steep banks, because cattail grows generally at depths less than 0.7 m (Squires and Van der Valk, 1992). Another factor, may be attributed to the fine granulometry of the sediment which does not allow good oxygenation of the roots (Ewing, 1986).

Sediment analyses from the Sloman and Quillagua sites showed average As concentrations of ~400 mg/kg and ~2000 mg/kg, respectively. The As concentrations in Quillagua sediments rank among the highest concentration of As known in the Loa River basin sediments (Romero et al., 2003). To date, the factors underlying the large differences between the two sites remain unknown.

3. Materials and methods

3.1. Description of the sites

The Sloman and Quillagua sites are located in the Lower Loa (Fig. 1). The Sloman site is located at 920 m above sea level (masl),

it has a surface area of 0.1 km² and it extends from 21°51'26.8"S, 69°31'4.6"W to 21°51'13.1"S, 69°30'52.0"W. The Quillagua site (806 masl) is located 23 km downstream from the Sloman site. It has a surface area of 3 km² encompassing from 21°41'6.0"S, 69°31'41.7"W to 21°38'29.5"S, 69°32'49.6"W.

3.2. In situ sampling and measurement methods

Sediment description and sampling campaigns were conducted at each site over three years (June 2007, July 2008 and December 2009). The values of pH, EC, temperature and dissolved oxygen (DO) in the flowing water were measured for each campaign using a multiparameter probe (HACH HQ40d, Hach Company, CO, USA) for 24 hour lapses. Water and sediment samples were collected from five points at each site (Fig. 1). Water samples of Sloman ($n = 6$) and Quillagua ($n = 30$) were filtered on-site using a 0.45 μ m cellulose acetate filter (Millipore Corporation, MA, USA). Water samples were acidified to pH <2 with

Table 1
The modified Tessier sequential extraction.

Step	Extractant	Target phase
E1	8 mL, 1 M of MgCl ₂ , pH 7, 25 °C	Exchangeable
E2	8 mL, 1 M of NaAc/HAc, pH 5, 25 °C	Bound to carbonates
E3	20 mL, 0.04 M of NH ₂ OH·HCl to 25% HAc, pH 2, 96 °C	Bound to Fe and/or Mn
E4	3 mL 0.02 M of HNO ₃ + 5 mL H ₂ O ₂ 30%, pH 2, 2 h, 85 °C 3 mL of H ₂ O ₂ 30%, pH 2, 3 h, 85 °C ollowed in cold, add 5 mL of 3.2 M NH ₄ Ac in HNO ₃ 20%, dilute to 20 mL in water, 0.5 h, 25 °C	Bound to OM
E5	EPA3050B	Residual

HNO₃ (Suprapure, Merck, Germany) and stored at 4 °C in polypropylene bottles until laboratory analyses were performed. Five sediment core samples at each site were collected using a Plexiglas cylindrical manual corer (3.2 cm diameter; 40 cm length). Sediment cores were sectioned in situ every 3 cm (as far of possible) and stored in plastic containers at <4 °C in the dark. Sediment samples were brought to the laboratory and were frozen until chemical analyses were performed. Core sections were grouped in surface and deeper sediments. Surface sediments considered two sections per sediment core for depths of 0–6 cm while deeper sediments considered at least six sections per core collected at depths of 6–50 cm. Overall, 20 and 29 sediment sections were analyzed from the Sloman and Quillagua sites, respectively. Aquatic plant samples of *S. americanus* (n = 9) were collected from five points at the Quillagua site (Fig. 1). Once collected, the plants were washed with river water to remove excess sediment from the roots. Plant samples were stored at 4 °C in plastic bags until chemical analyses were performed (generally less than one week).

3.3. Preparation and analysis

3.3.1. Pore water and sediments

Each sediment sample was divided into two sub-samples. The first sub-sample was oven dried at 40 °C for 2 days to eliminate moisture excess. A portion of this dried sample was used to measure the total water content (1 g of dry sediment at 105 °C for 16 h) and the remainder was sieved through a 2 mm mesh to remove roots and large sand particles before OM and elemental analyses were performed. OM was measured with the Walkley and Black's method (1934) and elemental composition was characterized with Total Reflection X-ray Fluorescence (TXRF) spectrometry. The second sub-sample underwent interstitial water extraction by centrifugation at 6000 rpm for 10 min. The extracted water was filtered through a 0.2 µm pore diameter nylon membrane for TXRF analysis.

Table 2
Parameters and elements in the water column from the Sloman and the Quillagua from this study (2007–2009), and the DGA monitoring station (2003–2011). The element concentration of DGA station corresponds to unfiltered samples.

Site	Author (sampling period)	n	Q (m ³ /s)	Temp. (°C)	pH	Cond. (mS/cm)	Oxygen	As	Ca	Fe	Mg	Mn	Sr	SO ₄	Br	B	COD	K	Na	Cl
							(mg/L)													
Sloman (920 masl)	This study (2007–2009)	6	–	16.2 ^a	8.4 ^a	15.4 ^a	11.6 ^a	2.11	306	0.23	227	0.04	11.82	–	1.91	29.0	18.7	151	2413	–
	Romero et al., 2003 (1999–2000)	2	–	16.0	8.1	14.4	–	2.40	410	–	240	–	10.15	815	–	35.5	–	–	2200	4300
Quillagua (806 masl)	This study (2007–2009)	30	–	14.3 ^a	8.0 ^a	16.4 ^a	6.0 ^a	1.82	339	0.28	271	0.04	12.26	–	1.81	32.3	N.D.	177	2659	–
	Romero et al., 2003 (1999–2000)	2	–	18.0	8.1	14.4	–	2.35	410	–	255	–	10.25	885	–	38.0	–	–	2350	4600
	DGA station (2003–2011). Annual mean	21	0.49 ^a	15.4	7.7	17.2	8.0	2.40	472	0.30	304	N.D.	–	1102	–	39.8	58.6	246	3103	5281

N.D., not detected; –, not measured.

^a The n for these parameters was n = 65 in This study and in DGA Station n = 128 (1998–2011).

3.3.2. Soil particle analysis procedure

The percentages of sand, silt, and clay particles in the sediment were estimated by feel (Lesikar et al., 2005). The sediment was rubbed between the fingers and the thumb and an estimate of the amount of the various separates present was made based on the degree to which the characteristic properties of each were expressed.

3.3.3. XRD analysis

Sediment mineralogy was characterized using powder X-Ray diffraction (D2 Phaser, Bruker AXS, Germany) in a silicon low-background sample carrier. Samples were dried at 40 °C, sieved through a 2 mm mesh and were micronized using an agate mechanical mill. The XRD measurement was performed at 30 kV and 10 mA using Cu-Kα radiation. Data analysis was performed using the EVA software (Bruker AXS, Germany).

3.3.4. Sequential extractions

The method of sequential extractions is often used to probe metal speciation and contaminant mobility in soils and sediments. The step-wise chemical treatment and analysis of extracted solutions from the solid phase operationally define contaminant associations with specific chemical compartments in the solid (e.g., exchangeable fraction, carbonates, Fe/Mn oxides, organic matter, residual). Despite their limitations, sequential extractions are widely used, including Tessier et al. (1979) and BCR (Baig et al., 2009) methods. To estimate the association of As with OM in the Sloman and Quillagua sediments, a slightly modified Tessier sequential extraction procedure was implemented using the EPA3050B digestion method (USEPA, 1986) for the final step. Tessier's method was chosen because unlike other alternatives, one of its steps specifically targets OM and the procedure is still widely used (Koretsky et al., 2008; Luo et al., 2012; Mílačič et al., 2012). For the extraction analysis, 1 g of each dried (at 40 °C) sediment sub-sample was used. The chemical extractants and corresponding target phases are shown in Table 1. To confirm the recovery rate of the total extracted As in the five extraction steps, the original sample was treated by using the EPA3051A method (USEPA, 1997). The accuracy of the sequential chemical extraction was determined by comparing the sum of the concentrations obtained at different stages of extraction (E1 to E5) with the contents obtained by total decomposition using the EPA3051A method. The accuracy values ranged between 70% and 81% (Table 7), which are of the same order as those obtained by other researchers (Favas et al., 2011).

3.3.5. Plants

The *S. americanus* samples (n = 9) collected at the Quillagua site were cut in the laboratory to separate the roots from the stems (leaves included). These samples were carefully washed in distilled water and then dried at room temperature. A portion of the root

and stem was dried at 70 °C for 2 days to estimate the dry weight (d.w.). Another portion was ground using an agate mortar and pestle. Approximately 3 g of the ground material was incinerated in a muffle furnace with an ascending temperature ramp of 250 °C to 500 °C over a 2 h period. A 20 mg aliquot of the resulting ash was used for elemental analysis with TXRF.

3.3.6. TXRF analysis

TXRF measurements were made with a Bruker S2 PICOFOX TXRF (Bruker AXS, Germany). The excitation parameters were 50 kV and 750 mA. All of the samples were measured for 300 s at least in triplicate. The spectra were evaluated using the Spectra software (Bruker AXS, Germany). TXRF was deemed a convenient technique because it has been successfully used for water and sediment analysis (Stosnach, 2005, 2006), it needs small sample amounts, and it requires minimal sample preparation. Furthermore, a clear advantage in sediment analysis is that TXRF measurements are not biased by the presence of refractory phases during acid digestions. Since measurements are done over a very thin layer of the sample, matrix effects found in X-ray fluorescence are negligible in TXRF measurements.

The quantitative TXRF analysis was conducted by addition of an internal Ga standard of known concentration. For solid samples (sediment and plant samples), 20 mg of finely ground material (<75 µm) was dispersed in 1 mL of Triton X-100 (Calbiochem) solution at 1%. A variable volume of standard Ga solution (1000 mg/L, Merck) was added to each dilution. For aqueous samples, 500 µL of the sample was mixed with 500 µL of HPLC quality water (Merck). A variable volume of standard Ga solution was added to each diluted solution (100 mg/L). Finally, 10 µL of each solid sample in suspension or a diluted aqueous sample was taken and placed in the center of the TXRF sample holder, where it was dried on a heating plate at 40 °C for later analysis. The TXRF measurements were confirmed by using traditional acid digestion + ICP-OES on a subset of the same samples. The accuracy (recovery) and precision (relative standard deviation) of the elemental quantification by TXRF were tested by measuring and comparing with the standard solution (Merck XVI, 250 µg L⁻¹). TXRF results for As, Fe, Ca, Sr and Mn did not differ significantly from the values reported according to the analysis of variance (ANOVA) test at the 95% confidence interval.

3.3.7. ICP-OES

Inductively coupled plasma optical spectrometry (ICP-OES) was performed (iCAP 6300; Thermo Fisher Scientific, Waltham, MA, USA) in selected water samples and to confirm the results from TXRF analysis on digested water and sediment samples.

3.4. Statistical analysis

The element concentrations in plants, sediments, water and the parameters pH, EC, temperature, flow data, depth and OM were statistically evaluated by correlation analysis with the MINITAB® software (version 14) or by statistical non-parametric Kruskal–Wallis analysis of variance. Cluster analysis was conducted with the R statistical software (R Development Core Team, 2008). The Pearson coefficient was used with a 95% confidence threshold ($p < 0.05$) for both analyses.

4. Results and discussion

The dissolved element concentrations in the surface water at the Sloman and Quillagua sites (such as As, Ca, Fe, Mg, Sr, Br, B, K, Na and Cl) are shown in Table 2, while DO and pH differed between the two sites. The concentration of oxygen at the Sloman and Quillagua sites showed that they are well oxidic (11.6 and 6 mg/L respectively). The continuous measurements taken over 24 h at each site showed that the oxygen concentrations measured by the luminescent probe varied throughout the day with higher values at the Sloman site (mean = 11.6, min = 7.9 and max = 14.8 mg/L) compared to those at the Quillagua site (mean = 6.0 mg/L), where the DO levels fluctuated with the lowest reading during the night (1.2 mg/L) and highest reading at noon (11.5 mg/L) well above saturation. The measured DO concentrations above saturation values point to the role of photosynthetic activity at both sites. The dissolved organic carbon (DOC) at the Sloman site was 18.7 mg/L while it was lower at the Quillagua site (undetected), which can be attributed to a predominant phytoplankton biomass role at the Sloman site and cyclic photosynthetic activity of macrophytes at the Quillagua site.

Table 2 shows the averages of relevant water quality parameters ($n = 21$, 2003–2011) and annual mean flow data ($n = 128$, 1998–2011) reported by the Chilean Water Agency (DGA) for the monitoring station near Quillagua. When contrasted with the result of this study, the Sloman and Quillagua present ranges of reported parameters are As: 1.8–2.1 mg/L; Fe: 0.23–0.28 mg/L; Mn: 0.04 mg/L; K: 151–177 mg/L; Na: 2413–2659 mg/L; and Ca: 306–339 mg/L. These values are consistent with previous measurements of DGA and Romero et al. (2003), although As shows slightly higher concentrations. This difference may be attributed to either different sampling time.

To identify elemental associations in the flowing water and their relationship with the river flow, monthly averages over 2003–2011 from the DGA data set were analyzed. The correlation analysis between average flows and elemental concentrations (Table 3) suggested a dilution effect for high flows (e.g., Cl behavior), while higher flows are positively correlated with higher As and Fe concentrations, pointing to mobilization of As, Fe rich sediments during high flow events. Further, the

Table 3

Correlation analysis on water quality parameter for Quillagua. The value of the correlation coefficient r is reported for the available DGA monitoring station data (2003–2011, $n = 21$).

	Q	Temp.	pH	Cond.	Oxygen	As	Ca	Fe	Mg	SO ₄	B	COD	K	Na
Temp.	−0.17													
pH	0.061	0.080												
Cond.	−0.28	0.251	−0.09											
Oxygen	0.014	−0.29	0.013	0.356										
As	0.762**	0.188	0.242	−0.19	−0.22									
Ca	−0.180	0.267	−0.11	0.497*	−0.28	0.13								
Fe	0.702*	0.031	0.064	−0.18	−0.41	0.879**	0.13							
Mg	−0.621*	0.504*	−0.08	0.782**	−0.05	−0.29	0.566*	−0.25						
SO ₄	−0.21	0.259	−0.04	0.644*	−0.04	−0.01	0.541*	0.061	0.738**					
B	−0.45	0.522*	0.009	0.635*	−0.05	−0.07	0.483*	−0.18	0.808**	0.445				
COD	−0.25	0.531*	0.056	0.385	−0.44	0.157	0.496*	0.21	0.753**	0.808**	0.490*			
K	−0.31	0.323	−0.01	0.542*	−0.12	−0.18	0.33	−0.06	0.736**	0.792**	0.362	0.823**		
Na	−0.44	0.498*	−0.2	0.754**	0.014	−0.17	0.478*	−0.15	0.812**	0.364	0.824**	0.56*	0.536*	
Cl	−0.590*	0.497*	−0.15	0.815**	−0.01	−0.27	0.642*	−0.23	0.968**	0.704*	0.865**	0.679*	0.626*	0.833**

* $p < 0.05$.

** $p < 0.001$.

Table 4

Average and standard error of element concentrations and %OM in sediments from Sloman and the Quillagua sites. The “0–6”, “6–50”, and “Total” labels correspond to the surface sample, the deep sample, and the total sample (surface + deep) averages, respectively. Measurement uncertainties are a smaller component of the standard error compared to spatial heterogeneity as a source of variability.

Site	n	Depth (cm)	OM (%)	As	Ca	Sr	Fe	Mn	S	Br
mg/kg d.w.										
Sloman	12	0–6	2.4 ± 0.6	262 ± 35	56,873 ± 7744	756 ± 85	24,555 ± 2119	559 ± 33	5558 ± 1701	11.4 ± 3.5
	8	6–50	1.9 ± 0.2	335 ± 46	82,429 ± 13,813	870 ± 137	17,256 ± 4447	563 ± 67	1255 ± 219	7.3 ± 0.8
	20	Total	2.2 ± 0.3	292 ± 28	67,096 ± 7563	801 ± 74	21,636 ± 2269	561 ± 32	3837 ± 1116	9.7 ± 2.1
Quillagua	8	0–6	6.2 ± 1.4	1528 ± 395	36,636 ± 3048	492 ± 52	21,028 ± 3390	864 ± 216	1587 ± 539	34.8 ± 9.1
	21	6–30	0.9 ± 0.1	155 ± 11	38,163 ± 2098	342 ± 19	12,956 ± 593	235 ± 10	1176 ± 293	2.8 ± 0.4
	29	Total	2.3 ± 0.6	534 ± 156	37,742 ± 1713	384 ± 24	15,183 ± 1200	409 ± 78	1290 ± 257	11.7 ± 3.6

concentration of Fe and As is strongly correlated ($r = 0.88$, $p < 0.001$), suggesting Fe–As association, presumably as As bound to HFO in the suspended solids.

The soil particle analysis procedure indicate that samples from Quillagua were typically coarse-textured, dominated by medium and fine sand. In contrast, Sloman samples were fine-textured, dominated by a mixture of silt and clay particles, which is consistent with the sedimentation basin effect of the dam. On the other hand, the XRD analysis of the sediments from the Sloman and Quillagua sites showed similar mineralogical compositions, including quartz, calcite, birnessite, phyllosilicate minerals (e.g., muscovite, illite), and feldspars (view supporting information for XRD analyses). Evidence of As-bearing minerals within the collected XRD was not found, suggesting that if As solid phases were present in the sediment, they were either XRD-amorphous or they were in such a small quantity that rendered them non detectable.

Quantitative analysis showed heterogeneity in the concentrations and vertical distribution of elements and OM in sediments of the Sloman and Quillagua sites (Table 4). Considering all the strata in the cores, the Sloman sediments had an average As concentration of 292 ± 28 mg/kg d.w., a value almost one half of that measured at Quillagua (534 ± 156 mg/kg d.w.). The Sloman site was found to contain similar As concentrations in the surface strata (0 to 6 cm; 262 ± 35 mg/kg d.w.) compared to the deeper strata (6 to 50 cm; 335 ± 46 mg/kg d.w.). In contrast, the average As concentrations in surface strata at Quillagua was 1528 ± 395 mg/kg d.w., meanwhile ~10 times lower As concentrations were found in deeper strata (155 ± 11 mg/kg d.w.). A similar pattern was found with OM distribution in sediments. Considering all the strata in the cores, the Sloman sediments have an average OM concentration of $2.2 \pm 0.3\%$, a value similar to that measured at Quillagua ($2.3 \pm 0.6\%$). The Sloman site was found to contain similar OM concentrations in the surface strata

($2.4 \pm 0.6\%$) compared to the deeper strata ($1.9 \pm 0.2\%$). In contrast, the average OM concentrations in surface strata at Quillagua were $6.2 \pm 1.4\%$, while ~6 times lower OM concentrations were found in deeper strata ($0.9 \pm 0.1\%$). Consequently, the Quillagua site (the site with abundant macrophytes) shows a noticeable surface enrichment for As and OM.

A similar occurrence pattern to that of As and OM was observed for Fe, Mn, and Br, as shown in Table 4. At Sloman, Fe concentrations in surface and deep strata were $24,555 \pm 2119$ mg/kg d.w. and $17,256 \pm 4447$ mg/kg d.w., respectively; while for Quillagua they were $21,028 \pm 3390$ and $12,956 \pm 593$ mg/kg d.w., respectively. The average Mn concentrations in Sloman and Quillagua sediments were comparable (561 ± 32 mg/kg d.w. and 409 ± 78 mg/kg d.w. of Mn, respectively). At Sloman, Mn concentrations were similar in surface and deeper strata (559 ± 33 mg/kg d.w. vs. 563 ± 67 mg/kg d.w. of Mn, respectively), while Mn concentrations at Quillagua were ~4 times higher in the surface strata compared to the deeper strata (864 ± 216 mg/kg d.w. vs. 235 ± 10 mg/kg d.w. of Mn, respectively). Similarly, Sloman and Quillagua had comparable average Br concentrations (9.7 ± 2.1 mg/kg d.w. vs. 11.7 ± 3.6), but Quillagua had ~12 times higher Br concentrations in the surface strata (34.8 ± 9.1 mg/kg d.w.) compared to the deeper strata (2.8 ± 0.4 mg/kg d.w.).

Ca and Sr showed a completely different occurrence pattern compared to As, OM, Fe, Mn, and Br. Ca and Sr concentrations were higher in Sloman sediments compared to Quillagua sediments and showed different distribution patterns. The Sloman site contained $67,096 \pm 7563$ mg/kg d.w. of Ca and 801 ± 74 mg/kg d.w. of Sr, roughly twice the average concentrations measured at Quillagua ($37,742 \pm 1713$ and 384 ± 24 mg/kg d.w., respectively).

Consistent findings were obtained from the cluster dendrogram and correlation analysis performed on the results of the chemical analyses of

Table 5

Correlation analysis of selected elements and depth from all sediment samples for Sloman ($n = 20$) and Quillagua ($n = 29$). Correlation coefficients r are shown.

	Depth	OM	As	Ca	Sr	Fe	Mn	S
Sloman								
OM	–0.303							
As	0.172	0.278						
Ca	0.186	0.303	0.633**					
Sr	–0.072	0.468*	0.540*	0.932**				
Fe	–0.139	–0.283	–0.374	–0.813**	–0.715**			
Mn	0.149	–0.189	0.188	–0.107	–0.090	0.465*		
S	–0.160	–0.129	–0.491*	–0.302	–0.179	0.409	0.312	
Br	–0.410	0.869**	0.069	0.125	0.342	–0.189	–0.227	–0.110
Quillagua								
OM	–0.569**							
As	–0.611**	0.852**						
Ca	–0.092	–0.015	–0.047					
Sr	–0.524**	0.755**	0.677**	0.614**				
Fe	–0.337	0.819**	0.715**	–0.191	0.540**			
Mn	–0.539**	0.875**	0.912**	0.005	0.736**	0.842**		
S	–0.176	0.341	0.245	–0.182	0.187	0.285	0.320	
Br	–0.601**	0.932**	0.834**	0.075	0.764**	0.722**	0.778**	0.252

* $p < 0.05$.

** $p < 0.001$.

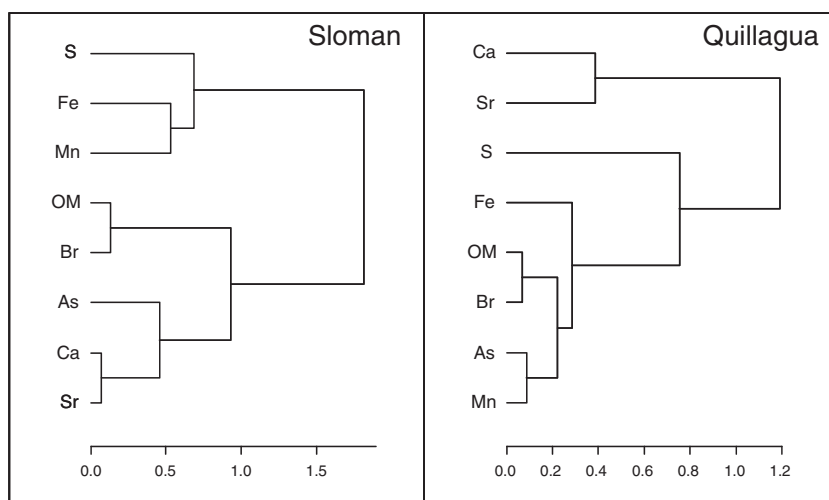


Fig. 2. Cluster dendrogram analysis for elements and organic matter in all sediment samples from the Sloman ($n = 20$) and the Quillagua ($n = 29$) sites.

all sediment samples from Sloman ($n = 20$) and Quillagua ($n = 29$) (Table 5 and Fig. 2). At Quillagua, As clustered and was correlated directly with Mn, OM, Br, and Fe, while at Sloman As clustered and was correlated directly only with Ca and Sr. These results suggest differential As binding and associations at both sites with a strong As enrichment on surface sediments at Quillagua.

The As distribution at the Sloman site was correlated with Ca ($r = 0.63$, $p < 0.001$) and Sr ($r = 0.54$, $p < 0.05$), while the As distribution at the Quillagua site was correlated with Mn ($r = 0.91$, $p < 0.001$), OM ($r = 0.85$, $p < 0.001$), Br ($r = 0.83$, $p < 0.001$) and Fe ($r = 0.72$, $p < 0.001$). At Sloman a negative correlation between the distribution of As and S ($r = -0.49$, $p < 0.05$) was observed, which was not found at Quillagua ($r = 0.25$, $p > 0.05$). The result of negative correlation found between As and S in sediments, the high As concentration in pore water in shallow Sloman sediments (1.4 ± 0.6 mg/L), and the high content of S on surface sediments of Sloman (5558 mg/kg d.w.) may be an indication of the oxidation of sulfide minerals and a limited sorption capacity towards As compared to Quillagua, where the Fe and Mn oxides in the solid phase strongly bind As from the pore waters. Despite Sloman showing a similar content of Fe in sediments compared to Quillagua, a correlation of Fe with As ($r = -0.37$, $p = 0.104$) was not found at the Sloman site. This implies that the driving conditions necessary to allow the association between As and Fe are absent in Sloman in comparison to Quillagua where that association was significant ($r = 0.715$, $p < 0.001$). Instead, in Sloman As co-occurs with Ca and Sr. The more alkaline conditions at Sloman ($\text{pH} = 8.4$) compared to Quillagua ($\text{pH} = 8$) tend to further limit the affinity of As towards sorption sites on the Fe oxy-hydroxides (Smedley and Kinniburgh, 2002). Conversely, under calcareous and alkaline environments, carbonate can become important As sorbents (Sadiq, 1997). Goldberg and Glaubig (1988) and Sørensen et al. (2008) showed that calcite adsorbs As (V) under oxic alkaline laboratory conditions. Thus, the significant correlation between Ca and Sr with As at the Sloman site could result from adsorption and coprecipitation with carbonates. In contrast, at the Quillagua site, the strong correlation between As and Mn, OM, Br and Fe and the enrichment of these elements in the surface strata

strongly suggests that Fe oxyhydroxides associated to plant roots within an OM rich setting controls As partition. These analyses are consistent with scanning electron micrographs and energy dispersive spectroscopic analyses performed on plant roots found at Quillagua (information presented in SEM-EDX Supplementary Information).

The results regarding the As–OM association and correlation are consistent with previous research. Meharg et al. (2006) reported that As was codeposited with organic carbon in the Bengal Delta (India). Wang et al. (2010) found a positive correlation between As and OM and Fe in sediment from the Pearl River (China). Similarly, García-Sánchez et al. (2010) reported that the presence of OM in soils from mining areas impacted As distribution. The enrichment of As associated with Fe oxides and OM is likely to occur in the presence of aquatic vegetation and Fe. This mechanism competes with As and Fe release under reducing conditions due to organic carbon oxidation catalyzed by microbial activity (Ahmann et al., 1997; Cosgrove, 1970; Islam et al., 2004). Consequently, the processes driving As enrichment and release at these two Loa River sites show similarities with those described for the Bengal Delta.

The strong correlation between OM and Br for Sloman (0.869, $p < 0.01$) and Quillagua (0.932, $p < 0.01$) sediments is consistent with previous works that observed that Br is associated with detrital OM (Kabata-Pendias and Pendias, 2001; Rao et al., 2008). It has been observed that Br reacts quickly with natural organic matter to form bromide and organo-bromine species (Song et al., 1996). Thus Br clustering with As is likely the result of Br association with OM.

The elemental analysis of pore water (Table 6) from both sites indicated that the Sloman site had a higher dissolved concentration of As (1.4 ± 0.6 mg/L), Ca (805 ± 90 mg/L), Sr (38.7 ± 8.1 mg/L), S (676 ± 56 mg/L) and Br (9.8 ± 2.5 mg/L) than that of the Quillagua site, corresponding to 0.5 ± 0.1 mg/L of As, 612 ± 49 mg/L of Ca, 23.2 ± 1.4 mg/L of Sr, 567 ± 50 mg/L of S and 3.5 ± 0.1 mg/L of Br, respectively.

The results from Tessier sequential extractions (Table 7) were consistent with the cluster and correlation analyses at both sites. Sloman and Quillagua sediments contained similar proportions of the

Table 6
Element concentrations in the sediment pore-water.

Site	n	Depth (cm)	As	Ca	Sr	Fe	Mn	S	Br
mg/L									
Sloman	9	0–50	1.4 ± 0.6	805 ± 90	38.7 ± 8.1	1.4 ± 0.7	0.2 ± 0.1	676 ± 56	9.8 ± 2.5
Quillagua	16	0–30	0.5 ± 0.1	612 ± 49	23.2 ± 1.4	1.9 ± 0.6	0.8 ± 0.3	567 ± 50	3.5 ± 0.1

Table 7

Tessier's sequential extraction of As on cores S5 and Q3 of Sloman and Quillagua respectively. The values show average and standard deviations.

Depth (cm)	n	Ionic		Carbonates		Ox. Fe/Mn		Organic matter		Residual		Totals (mg/kg d.w.)	EPA3051A (mg/kg d.w.)	
		E1	(%)	E2	(%)	E3	(%)	E4	(%)	E5	(%)			
		(mg/kg d.w.)		(mg/kg d.w.)		(mg/kg d.w.)		(mg/kg d.w.)		(mg/kg d.w.)				
<i>Sloman</i>														
S5 (0–6)	3	14 ± 6.4	3 ± 1.3	31 ± 9.9	9 ± 3.9	339 ± 211	58 ± 16	26 ± 5.7	7 ± 1.6	71 ± 4.0	23 ± 9.7	483 ± 227	690 ± 350	
S5 (6–50)	4	11 ± 2.0	3 ± 0.6	26 ± 3.6	6 ± 0.6	376 ± 116	68 ± 11	26 ± 4.0	6 ± 0.9	65 ± 21.6	18 ± 8.9	505 ± 102	622 ± 143	
Total	7	13 ± 2.7	3 ± 0.6	29 ± 4.2	7 ± 1.6	360 ± 101	64 ± 9	26 ± 3.0	6 ± 0.8	68 ± 11.7	20 ± 6.1	495 ± 102	651 ± 153	
<i>Quillagua</i>														
Q3 (0–6)	2	22 ± 0.4	2 ± 0.2	18 ± 1.7	1 ± 0.2	943 ± 31	66 ± 4	257 ± 101	17 ± 5.3	207 ± 13	14 ± 0.5	1446 ± 143	2056 ± 358	
Q3 (6–30)	7	10 ± 0.6	3 ± 0.2	23 ± 1.3	8 ± 1.1	157 ± 20	52 ± 3	18 ± 1.8	6 ± 0.3	86 ± 5.7	30 ± 1.5	295 ± 25	373 ± 35	
Total	9	13 ± 1.8	3 ± 0.3	22 ± 1.3	7 ± 1.4	332 ± 117	55 ± 3	71 ± 39	9 ± 1.9	113 ± 18.4	26 ± 2.5	551 ± 172	747 ± 256	

total extracted As associated with the exchangeable (step E1; 3%) and carbonate (step E2; 7%) fractions, although the Sloman sediments contained higher concentrations of more easily leachable As (E1 + E2) compared to the Quillagua sediments, corresponding to 42 mg/kg d.w. of total As (that is $13 \pm 2.7 + 29 \pm 4.2$ mg/kg d.w.) and 35 mg/kg (that is $13 \pm 1.8 + 22 \pm 1.3$ mg/kg d.w.), respectively.

The results of the last As extractions steps associated to Fe–Mn oxides (step E3) and OM (step E4) are consistent with the As association patterns with OM, Mn, Fe and Br described earlier (Table 4). For step E3, considering all profiles and strata, the average of As associated to Fe and/or Mn in Sloman and Quillagua was very similar (360 ± 101 mg/kg d.w. and 332 ± 117 mg/kg d.w., respectively). When the surface and the deeper sediment strata were compared, the As in step E3 had the same order of magnitude for the Sloman site, in the surface strata vs. the deeper strata (339 ± 211 vs. 376 ± 116 mg/kg d.w., respectively). At the Quillagua site, the As concentration extracted in step E3 was ~3 times higher in the surface samples compared to the deeper strata (943 ± 31 vs. 157 ± 20 mg/kg d.w., respectively).

For step E4 (the step that targets As associated with OM), Quillagua showed ~10 times higher As concentrations being extracted from the surface strata compared to Sloman (257 ± 101 vs. 26 ± 5.7 mg/kg d.w.). This fraction represented the second highest proportion of the total As (the first is E3) that was extracted from the sediments ($17 \pm 5.3\%$ vs. $7 \pm 1.6\%$, respectively).

Finally, a greater As concentration associated with more recalcitrant minerals (step E5) was observed at the Quillagua site compared to the Sloman site (113 ± 18.4 vs. 68 ± 11.7 mg/kg d.w.), but represented a similar proportion (26 ± 2.5 vs. $20 \pm 6.1\%$, respectively) of the total extracted As.

Consequently, the sequential extraction analyses suggest that the As concentration in the sediments was driven by different chemical and biological mechanisms at each site. These differences resulted in a higher proportion of As leachable by neutral and acid solutions at the Sloman site compared to the Quillagua site (steps E1 + E2). At the Sloman site, the relative As binding affinity to different phases based on the total content is: Fe/Mn > residual > carbonates > OM > exchangeable, while at Quillagua the order is: Fe/Mn > residual > OM > carbonates > exchangeable. For the surface strata in Quillagua, the As extractions follows: Fe/Mn > OM > residual > exchangeable > carbonates, which is consistent with

the clustering analysis. This suggests that OM is a key factor for the accumulation and distribution of As in the surface sediments in Quillagua. Comparatively, these results indicate that OM contributes more effectively to As immobilization at Quillagua, than carbonates do at Sloman.

However, there is an inconsistency with respect to the association between As and Fe when comparing the results from sequential extractions with the cluster and correlation analysis. While the cluster analysis and correlation analyses suggest greater As co-occurrence with Ca at Sloman, the sequential extraction shows greater association of As with Fe/Mn oxides. This discrepancy is likely due to the rapid oxidation of Fe during the sample manipulation process (Chen et al., 2005), despite the steps were taken to minimize this potential source of error. The rapid oxidation of Fe during sequential extractions can induce misleading results. Thus, the Tessier sequential extractions are likely to over-estimate the As binding to Fe/Mn oxides. Although sequential extraction procedures including Tessier and BCR (the European Community Bureau of Reference three-step sequential extraction procedure) have extensively been used and evaluated to analyze element speciation in solid phases, further insights and resolution could be gained from other sequential extraction techniques like Keon et al. (2001) or synchrotron-based spectroscopic techniques (e.g., X-ray absorption spectroscopy).

Chemical analyses of roots and stem from macrophytes collected at the Quillagua site (Table 8) revealed that *S. americanus* accumulate As mainly in its roots (128 mg/kg d.w.) compared to stems (21.4 mg/kg d.w.). A high correlation between Fe and As in the roots was found ($r = 0.99$), which points to As binding with the root's Fe plaque. This mechanism has been observed for other plants in previous studies (Blute et al., 2004; Chen et al., 2005; Hansel et al., 2002). The Biological Absorption Coefficient (BAC) is a parameter used as a primary reference for quantifying the potential use of a plant as a remediation tool for a polluted soil. The BAC is the ratio of the target metal concentration in the plant foliage to that of the soil. Baker (1981) proposed that plants coping with metal toxicity through exclusion mechanisms are those with a $BAC \ll 1$. Based on the measured As concentrations on the plants and sediments, the estimated BAC for As of *S. americanus* was 0.03–0.05 (mean = 0.04), which places this plant among those using exclusion according to Baker (1981). Consequently, the iron plaque associated to the macrophytes plays a key role both as a process driving As enrichment in the surface sediment strata and also as a mechanism that helps the plants to lessen bioavailable As.

5. Conclusions

Fluvial sediments in the Loa River in northern Chile are enriched with As, a toxic element that constrain water uses in an extremely arid region. Quillagua and Sloman are two sites in the lower Loa watershed that have contrasting vegetation coverage, despite their proximity and similar water chemistries. Abundant vegetation in Quillagua is connected with differential As binding in the sediments

Table 8Concentrations and correlations of As and Fe content in *Scirpus americanus* samples from the Quillagua site.

<i>S. americanus</i>	n	As (mg/kg d.w.)		Fe (mg/kg d.w.)		Correlation	
		Mean	Range	Mean	Range	r	p-values
Roots	9	128	22–436	3628	728–11,556	0.99	0.000
Stems	9	21	16–27	108	133–430	0.95	0.014

compared to Sloman, highlighting a key factor that drives As mobility in fluvial systems.

Where plants are abundant (*S. americanus* in this case), the occurrence of As in sediments is chiefly associated to Mn, OM, and Fe. In that case, a preferential enrichment of As in surface sediments occurs likely due to an oxygenic environment that favors the formation of an Fe–Mn plaque with high affinity towards As. However, where vegetation is absent, lower and more uniform As concentrations are found in sediments, mainly associated to Ca and Sr, likely in the form of carbonates under this arid alkaline environment. Consequently, the differential As binding at these two sites is driven by contrasting biotic and abiotic processes.

Differential As binding implies different outcomes regarding As mobility: As associated to the coatings on the roots of the macrophytes is less mobile during the seasonal high flow events compared to the As in the fine sediments in Sloman. Furthermore, the establishment of thriving macrophyte populations is likely to foster As repositories along rivers. Nevertheless, the role of plants playing a significant role as As barriers to constrain As transport in this fluvial system is still debatable. Further studies determining As fluxes need to be conducted and key processes need to be carefully evaluated, including the dynamics of As association with plant surfaces during the plant cycle, or the fate of fine As-rich particles transported by the flowing water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2013.06.114>. These data include Google map of the most important areas described in this article.

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