Bull Environ Contam Toxicol (2011) 86:666–669
DOI 10.1007/s00128-011-0269-0

Total and Bioavailable Arsenic Concentration in Arid Soils and its Uptake by Native Plants from the Pre-Andean Zones in Chile

O. Díaz · Y. Tapia · R. Pastene · S. Montes ·
N. Núñez · D. Vélez · R. Montoro

Received: 1 December 2010 / Accepted: 29 March 2011 / Published online: 12 April 2011

Abstract Arsenic is the most important contaminant of the environment in northern Chile. Soil samples and plant organs from three native plant species, *Pluchea absinthioides*, *Atriplex atacamensis* and *Lupinus microcarpus*, were collected from arid zones in order to determine the total and bioavailable arsenic concentrations in soils and to assess the bioconcentration factor (BCF) and transport index (Ti) of arsenic in the plants. Total arsenic concentrations in soils (pH 8.3–8.5) where *A. atacamensis* and *P. absinthioides* were collected, reached levels considered to be contaminated (54.3 ± 15.4 and 52.9 ± 9.9 mg kg^{-1}, respectively), and these values were approximately ten times higher than in soils (pH 7.6) where *L. microcarpus* was collected. Bioavailable arsenic ranged from 0.18 to 0.42% of total arsenic concentration. In the three plant species, arsenic concentration in leaves were significantly ($p \leq 0.05$) higher than in roots. *L. microcarpus* showed the highest arsenic concentration in its leaves (9.7 ± 1.6 mg kg^{-1}) and higher values of BCF (1.8) and Ti (6.1), indicating that this species has a greater capacity to accumulate and translocate the metalloid to the leaf than do the other species.

O. Díaz (✉) · Y. Tapia · R. Pastene · S. Montes
Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile
e-mail: oscar.diaz@usach.cl

N. Núñez
Programa Agrícola de CODELCO, Calama, Chile

D. Vélez · R. Montoro
Instituto de Agroquímica y Tecnología de Alimentos (IATA), Apdo. 73, 46100 Valencia, Spain

Keywords Arsenic · Soil contamination · *Pluchea absinthioides* · *Atriplex atacamensis* · *Lupinus microcarpus*

Natural hydrogeological characteristics and the presence of volcanoes and mining activity are the most important sources of arsenic pollution in the water and soil in the Antofagasta Region of Chile (Queirolo et al. 2000). This region is dominated by arid soils, whose main characteristics include the absence of surface horizons and very low organic matter content. Arsenic concentrations in soils of this region can vary from 50 to 70 mg kg^{-1} (Muñoz et al. 2002). However, in general, the natural As concentration in soil varies between 5 and 6 mg kg^{-1}.

The normal As concentration in plants is usually <1 mg kg^{-1} and generally the As concentration in the root is higher than in the leaf (Madejón and Leep 2007; Moreno et al. 2008). Plants absorb As when it is in a bioavailable form. The bioavailable As fraction is chemically soluble, labile and readily available to plants; it is also makes up a small fraction of the total As concentration. Bioavailable As concentration depends on soil pH, organic matter content and oxides of Al, Fe, Mn and clay minerals (Fayiga et al. 2007).

Pluchea absinthioides, *Atriplex atacamensis and Lupinus microcarpus* are important native plants that constitute part of the desert scrub community of the pre-Andean area of the Antofagasta Region. In general, there are few published studies that have investigated the accumulation of As by the native vegetation growing in contaminated soils (Madejón and Leep 2007).

The objectives of the study were to: (1) Determine total and bioavailable arsenic concentrations in arid soils collected from different pre-Andean zones in Chile; and (2) Assess the ability of native plant species that grow in these soils (*P. absinthioides*, *A. atacamensis* and *L. microcarpus*) to accumulate As.

Materials and Methods

Native plants and soil samples were collected from three pre-Andean zones in the Region of Antofagasta (Chile) during December 2004. These zones were: (1) Chiu Chiu (22° 20′S, 68° 39′W, 2,526 m above sea level); (2) Lasana (22° 16′S, 68° 38′W, 2,667 m above sea level) and (3) Ayquina (22° 16′S, 68° 19′W, 3,005 m above sea level), located at 33, 45 and 74 km to the northeast of Calama city, respectively, (Fig. 1). The climate of the study zones is characterised by extreme aridity throughout the year (rainfall 5.7 mm per year) with very low relative humidity (average 33%); the average temperature is 20°C in summer and winter. Due to these unfavourable conditions, the presence of vegetation is scarce and therefore the number of individuals collected was limited.

Surface soil samples (0–20 cm depth) were collected in quadruplicate from the area adjacent to the plant roots. The pH was determined in aqueous extract 1:5. Percentage slit-clay was determined by weighing the soil retained on a sieve with a diameter >0.080 mm. Organic matter was determined by a colorimetric method using $K_2Cr_2O_7$, H_2SO_4 and saccharose solution as standard solutions. For a determination of total mineral elements, soil samples were dried at 40°C to constant weight, sieved to particle size of 2 mm and digested with aqua regia (HNO_3–HCl, 1:3). Total Ca, K, Mg, Cu, Fe, Mn and Zn concentrations were determined by atomic absorption spectrometry (AAS). To determine total N, the Kjeldahl method was used. Total P and S were determined by elemental analysis. Boron concentration was determined using a colorimetric method with azomethine after extraction with hot water. For determining total As concentrations in the soil, dry ashing mineralisation and quantification by flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) were employed. Bioavailable As concentration was measured by FI-HG-AAS after extraction with $NaHCO_3$. Detection limit of the apparatus is 0.006 $\mu g\ g^{-1}$ dw. Accuracy for Montana Soil (certified standard) found value = 98.19 ± 0.03 $\mu g\ g^{-1}$ (certified value = 105 ± 8 $\mu g\ g^{-1}$).

Three native plant species were collected in triplicate from their natural habitat: *Pluchea absinthioides* was collected from Chiu Chiu, *Atriplex atacamensis* was collected from Lasana and *Lupinus microcarpus* was collected from Ayquina. Plants were separated into leaves, stems and roots, dried at 60 ± 5°C until constant weight and then ground and sieved. Later samples were calcined and total As concentration was determined by FI-HG-AAS. All results are expressed in dry matter. The bioconcentration factor (BCF) and transport index (Ti) of As to the leaf were calculated using the following equations: BCF = As concentration in leaf/total As concentration in soil (mg kg^{-1}); and Ti = As concentration in leaf/As concentration in root (mg kg^{-1}).

The data were analyzed using single-factor ANOVA in the statistical program SPSS version 13.0. To test differences in bioavailable As concentrations between soil samples and total As concentrations between leaves, stems and roots, Duncan's test was used with a significance level of $p \leq 0.05$.

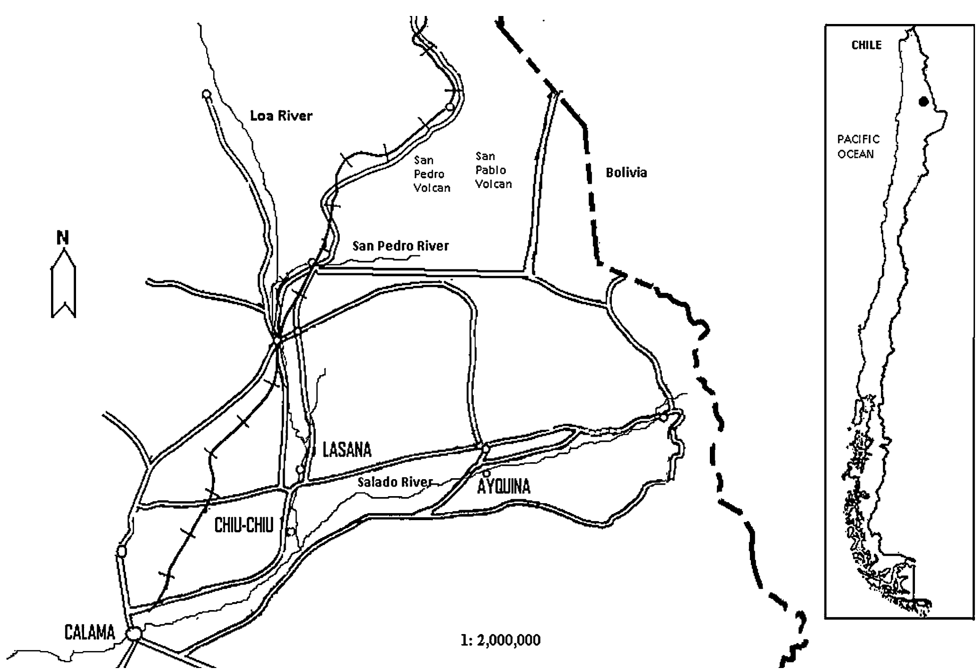

Fig. 1 Study areas, near the Loa river, where were collected soil samples and native plants (pre-Andean zone, Chile)

Results and Discussion

The pH for Chiu-Chiu and Lasana soil samples was similar (pH 8.5 and pH 8.3, respectively), while Ayquina soil had the lowest pH (pH 7.6; Table 1). Ayquina soil contained a higher percentage of silt–clay (4.33%) than soils from Chiu Chiu (2.66%) and Lasana (3.66%). In general, all of the soils were dominated by a sandy texture. Ayquina soil had a higher concentration of organic matter and of Ca, N, P and Fe than did Chiu-Chiu and Lasana soils. *L. microcarpus* is a nitrogen-fixing legume, which could explain the higher concentration of N in this soil. Levels of B, Cu, Mn and Zn are low in the three soils.

Total As concentration in soils ranged from 41.12 to 65.72 mg kg^{-1} (mean: 52.98 mg kg^{-1}) for Chiu-Chiu, from 32.59 to 68.23 mg kg^{-1} (mean: 54.34 mg kg^{-1}) for Lasana and from 4.24 to 7.28 mg kg^{-1} (mean: 5.58 mg kg^{-1}) for Ayquina. These results indicate that Chiu-Chiu and Lasana soils are contaminated with As, whereas Ayquina soils, with levels of As <6 mg kg^{-1}, are consistent with values for uncontaminated soils.

Bioavailable As concentrations in Chiu-Chiu and Lasana soils were 0.22 and 0.15 mg As kg^{-1}, respectively, which represented 0.42% and 0.27% of the total As concentrations, respectively. In Ayquina, the soil bioavailable As concentration was 0.01 mg kg^{-1}, which represented 0.18% of the total As concentration (Table 1). Chemical reactivity of As in solution is primarily controlled by surface reactions, specifically complexation with oxides/hydroxides of Al, Mn and especially Fe (Fitz and Wenzel 2002). Fe oxides are the primary adsorption sites for As in most soils and sediments, thereby decreasing its availability (Visoottiviseth et al. 2002). pH also is one of the main factors determining the bioavailability of As in contaminated soils (Fayiga et al. 2007). In general, high pH values (pH 8.6) increased bioavailable As in soil solution (Vázquez et al. 2008). In some cases, arsenic soil retention was observed to increase when organic matter (Balasoiu et al. 2001) and clay content were higher. The lowest bioavailable As concentration found in Ayquina soils may be associated with the low total concentration of As and higher organic matter and clay content than in Chiu Chiu and Lasana soils.

Table 1 Main physico-chemical soil characteristics and total and bioavailable arsenic concentrations (mg kg^{-1} dry matter) in soils

	Zones		
	Chiu-Chiu	Lasana	Ayquina
pH	8.5 ± 0.3	8.3 ± 0.3	7.6 ± 0.3
Slit-clay (%)	2.66 ± 1.5	3.66 ± 1.5	4.33 ± 1.1
Ca (%)	0.50 ± 0.34	0.87 ± 0.36	1.40 ± 0.14
K (%)	0.06 ± 0.02	1.04 ± 0.01	1.12 ± 0.16
Mg (%)	0.78 ± 0.33	1.55 ± 0.28	0.98 ± 0.03
N (%)	0.03 ± 0.02	0.02 ± 0.01	0.13 ± 0.07
P (%)	0.04 ± 0.01	0.04 ± 0.02	0.12 ± 0.02
As (mg kg^{-1})	52.98 ± 9.91	54.34 ± 15.43	5.58 ± 1.04
Bioavailable As (mg kg^{-1})	0.22 ± 0.09	0.15 ± 0.05	0.01 ± 0.005
B (mg kg^{-1})	0.23 ± 0.15	0.11 ± 0.01	0.02 ± 0.01
Cu (mg kg^{-1})	1.63 ± 1.18	0.27 ± 0.06	1.03 ± 0.32
Fe (mg kg^{-1})	13.63 ± 9.49	9.73 ± 5.22	16.66 ± 2.89
Mn (mg kg^{-1})	4.54 ± 0.60	4.23 ± 1.00	3.50 ± 1.04
Zn (mg kg^{-1})	1.00 ± 0.44	1.06 ± 0.64	0.33 ± 0.21

Values are means ± standard deviations, n = 4

Table 2 shows the dry weight and As concentration in leaves, stems and roots of *P. absinthioides*, *A. atacamensis* and *L. microcarpus* collected in different zones. Dry weight was similar between the species. Arsenic concentration in all species was significantly higher in leaves than in roots ($p \leq 0.05$). These results are uncommon because most plants preferentially accumulate As in their roots, and, even if they absorb high levels, transport of the metalloid to the aerial parts is minimal (Jedynak et al. 2009).

In general, As levels found in leaves of *P. absinthioides*, *A. atacamensis* and *L. microcarpus* (5.9–9.7 mg kg^{-1}) are high compared to other species. For example, in the herbaceous species *Cameroon angustifolium*, *Cirsium ssp*. and *Reseda luteola*, which were collected from soils (pH 7.3) with As levels similar to those found in Chiu Chiu and Lasana soils, As concentrations in leaves were between 1.01 and 2.90 mg kg^{-1} (Madejón and Leep, 2007). The highest As concentration in leaves was found in *L. microcarpus* (9.7 ± 1.6 mg kg^{-1}). However, As concentrations in Ayquina soils, where this plant species was collected, were lowest. Other researchers have also found high As levels in plants collected from soils with low As levels (Visoottiviseth et al. 2002).

Bioconcentration factor (BCF) was considerably higher in *L. microcarpus* (1.8) and >1 (Table 2), indicating that this species has an interesting ability to accumulate As. Some researchers have suggested that phytoextraction is feasible when the BCF is >1 (McGrath and Zhao 2003). Transport index (Ti) of As to leaves was >1 in all species, therefore plants accumulated As in the leaves (Table 2). *L. microcarpus* also reached the highest Ti, showing a remarkable ability to translocate As to the leaf.

The results indicate that total arsenic concentrations in arid soils of Lasana and Chiu-Chiu, where *Atriplex atacamensis* and *Pluchea absinthioides* were collected, respectively, reached pollutant levels. By contrast, in Ayquina soils, where *Lupinus microcarpus* was collected, As levels did not indicate pollution. The bioavailable arsenic concentration in Ayquina soils was lower than in Chiu-Chiu and Lasana soils; however, *Lupinus microcarpus*

Table 2 Dry weight (g) and As concentration (mg kg^{-1} dry matter), bioconcentration factor and transport index of As to the leaves

Native plant species	Plant organ	Dry weight (g)	As (mg kg^{-1})	BCF	Ti
P. absinthioides (Chiu-Chiu zone)	Leaf	2.7 ± 0.2	5.9 ± 1.0a	0.1	1.7
	Stem	2.8 ± 0.9	5.1 ± 0.4a		
	Root	2.6 ± 0.7	3.4 ± 0.2b		
A. atacamensis (Lasana zone)	Leaf	2.1 ± 0.9	6.3 ± 0.7a	0.1	3.7
	Stem	2.8 ± 0.7	2.5 ± 0.7b		
	Root	2.5 ± 0.7	1.7 ± 0.4b		
L. microcarpus (Ayquina zone)	Leaf	2.3 ± 0.3	9.7 ± 1.6a	1.8	6.1
	Stem	2.4 ± 0.5	2.5 ± 0.9b		
	Root	1.5 ± 0.2	1.6 ± 0.4b		

BCF bioconcentration factor, Ti transport index. Values are means ± standard deviation, n = 3. Different letters, in columns, indicate significant differences among organs of native plants species for As concentration, according to Duncan's test $p \leq 0.05$

showed the highest leaf As concentration (9.7 ± 1.6 mg kg^{-1} dry matter). For all three native plants, As concentrations were significantly higher in the leaves than in the roots. *Lupinus microcarpus* had the highest bioconcentration factor and transport index of arsenic to the leaf and therefore had a greater capacity to accumulate and translocate the metalloid. It would be interesting in future studies to evaluate the response of *Lupinus microcarpus* to soils contaminated with arsenic and to investigate its possible use in phytoextraction.

Acknowledgments This work was a collaboration between the Universidad de Santiago de Chile (USACH-DICYT), Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo (CYTED), Programa Agrícola de la Corporación del Cobre Chile (CODELCO), Instituto de Agroquímica y Tecnología de Alimentos (IATA-CSIC, Spain) and Dra. Pilar Bernal (CEBAS-CSIC, Spain).

References

Balasoiu C, Zagury G, Deschenes L (2001) Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition. Sci Total Environ 280:239–255

Fayiga AO, Ma LQ, Zhou Q (2007) Effects of plants arsenic uptake and heavy metals on arsenic distribution in an arsenic-contaminated soil. Environ Pollut 147:737–742

Fitz WJ, Wenzel WW (2002) Arsenic transformations in the soil-rhizosphere-plant system: fundamentals and potential application to phytoremediation. J Biotechnol 99:259–278

Jedynak L, Kowalska J, Harasimowicz J, Golimowski J (2009) Speciation analysis of arsenic in terrestrial plants from arsenic contaminated area. Sci Total Environ 407:945–952

Madejón P, Leep NW (2007) Arsenic in soil and plants of woodland regenerated on an arsenic-contaminated substrate: a sustainable natural remediation? Sci Total Environ 379:256–262

McGrath SP, Zhao FJ (2003) Phytoextraction of metals and metalloids from contaminated soils. Curr Opin Biotech 14:277–282

Moreno E, Peñalosa J, Carpena-Ruiz R, Esteban E (2008) Comparison of arsenic resistance in Mediterranean woody shrubs used in restoration activities. Chemosphere 71:466–473

Muñoz O, Díaz O, Leyton I, Núñez N, Devesa V, Suñer M, Vélez D, Montoro R (2002) Vegetables collected in the cultivated Andean area of Northern Chile: total and inorganic arsenic contents in raw vegetables. J Agric Food Chem 50:642–647

Queirolo F, Stegen S, Mondaca J, Cortés R, Rojas R, Contreras C, Muñoz L, Schwuger MJ, Ostapczuk P (2000) Total arsenic, lead, cadmium, copper, and zinc in some salt rivers in the northern Andes of Antofagasta, Chile. Sci Total Environ 255:85–95

Vázquez S, Carpena R, Bernal MP (2008) Contribution of heavy metals and As-loaded lupin root mineralization to the availability of the pollutants in multi-contaminated soils. Environ Pollut 152:373–379

Visoottiviseth P, Francesconi K, Sridokchan W (2002) The potential of Thai indigenous plant species for the phytoremediation of arsenic contaminated land. Environ Pollut 118:453–461