

# Phytostabilization of arsenic in soils with plants of the genus Atriplex established in situ in the Atacama Desert

Yasna Tapia Fernández • O. Diaz • E. Acuña • M. Casanova • O. Salazar • A. Masaguer

Received: 5 November 2015 / Accepted: 14 March 2016 / Published online: 22 March 2016 © Springer International Publishing Switzerland 2016

Abstract In the ChiuChiu village (Atacama Desert, Chile), there is a high concentration of arsenic (As) in the soil due to natural causes related to the presence of volcanoes and geothermal activity. To compare the levels of As and the growth parameters among plants of the same genus, three species of plants were established in situ: Atriplex atacamensis (native of Chile), Atriplex halimus, and Atriplex nummularia. These soils have an As concentration of  $131.2 \pm 10.4 \text{ mg kg}^{-1}$ , a pH of 8.6  $\pm 0.1$ , and an electrical conductivity of 7.06  $\pm 2.37$  dS m<sup>-1</sup>. Cuttings of Atriplex were transplanted and maintained for 5 months with periodic irrigation and without the addition of fertilizers. The sequential extraction of As indicated that the metalloid in these soils has a high bioavailability (38 %), which is attributed to the alkaline pH, low organic matter and Fe oxide content, and sandy texture. At day 90 of the assay, the As concentrations in the leaves of A. halimus  $(4.53 \pm 1.14 \text{ mg kg}^{-1})$  and A. nummularia  $(3.85 \pm 0.64 \text{ mg kg}^{-1})$  were significantly higher than that in A. atacamensis  $(2.46 \pm 1.82 \text{ mg kg}^{-1})$ . However, the three species accumulated higher levels of As in their

#### O. Diaz

#### A. Masaguer

Departamento de Producción Agraria, Universidad Politécnica de Madrid, CP 28040 Madrid, Spain

roots, indicating a phytostabilization capacity. At the end of the assay, *A. halimus* and *A. nummularia* generated 30 % more biomass than *A. atacamensis* without significant differences in the As levels in the leaves. Despite the difficult conditions in these soils, the establishment of plants of the genus *Atriplex* is a recommended strategy to generate a vegetative cover that prevents the metalloid from spreading in this arid area through the soil or by wind.

**Keywords** Saltbush · Arid area · Bioavailability · Sequential extraction

## Introduction

Northern Chile is a geographic area with a high concentration of arsenic (As) in soil and water that is attributed to a natural origin, as it is related to the presence of volcanoes and geothermal activity (Cáceres et al. 1992; Queirolo et al. 2000; Bundschuh et al. 2012). The village of ChiuChiu (2500 m a.s.l., Pre Andean area) is located in the Atacama Desert and is characterized by its extremely arid climate (5.0 mm of rainfall per year), the presence of winds of moderate to high intensity, the partial influence of summer rainfall, and the presence of the Loa and Salado Rivers, which facilitate the development of desert vegetation (Saiz et al. 2000). The main characteristic of this arid area is the absence of topsoil and organic matter (Sánchez and Morales 2004). The soils in the village of ChiuChiu are of high salinity and have an alkaline pH, and the As concentrations can

Y. T. Fernández (⊠) · E. Acuña · M. Casanova · O. Salazar Departamento de Ingeniería y Suelos, Universidad de Chile, Santa Rosa 11315, 8820808 Santiago, Chile e-mail: yasnatapiafernandez@gmail.com

Departamento de Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile

vary between 17 and 111 mg kg<sup>-1</sup> (Pizarro et al. 2003; Tapia et al. 2013a). The levels of As commonly found in soils generally ranged from 0.1 to 55 mg kg<sup>-1</sup> (Alloway 2010). Arsenic is a toxic metalloid without a known biological function in plants and behaves as an anion similar to phosphorus. Its mobility increases under alkaline conditions. Arsenic can be retained in soils by clay minerals, organic matter, and oxides, particularly those of Fe (Moreno et al. 2012).

The native flora in the village of ChiuChiu is predominantly formed by the so-called tropical inner desertic scrub, which consists of *Atriplex atacamensis*, *Tessaria absinthioides*, and *Distichlis spicata* (Luebert and Pliscoff 2006). Other native species, such as *Cortaderia atacamensis*, *Schinus molle*, and *Lycium humile*, also grow in these soils (Poblete et al. 1991; Latorre et al. 2006; Riedemann et al. 2006).

Although this geographical area is known worldwide for its high concentration of As (Bundschuh et al. 2012), few investigations have reported the concentration of this metalloid in native plants (Díaz et al. 2011), and there are no in situ studies related to the establishment of plants in this area. The soil has low economic importance for agriculture due to the climatic characteristics of this zone; however, some human communities of "atacamañena" ethnicity of the ChiuChiu village have small plots with *Daucus carota* (carrot) as the primary crop.

The Atriplex genus belongs to the Chenopodiaceae family, which is distributed worldwide and one of the most important families in North Chile (Poblete et al. 1991; Saiz et al. 2000). Many plants of this family are halophytes and xerophytes with an acid metabolism and C4 photosynthesis, which is an adaptive mechanism of plants that grow in deserts and arid areas (Akhani et al. 1997). The plants of the genus Atriplex have a high potential for rehabilitating degraded arid soils (Le Houérou 1992; Mendez et al. 2007) and have been recommended for the revegetation of mining soils (Lutts et al. 2004; Clemente et al. 2012; Pérez-Esteban et al. 2013), particularly the species A. halimus (Walker et al. 2014). Some species, such as A. nummularia and A. halimus, are used for animal feed in arid areas (Abu-Zanata et al. 2004); thus, their establishment in soils with high levels of metals/metalloids should consider protective measures to prevent pollution from being passed through the food chain. In Chile, A. halimus and A. nummularia were introduced between 1970 and 1979 to produce forage and fuel wood (Lailhacar et al. 1991; Lailhacar et al. 1995). The introduction of these species had beneficial effects on the ecosystem (Lailhacar and Torres 2001; Figueroa et al. 2004).

In most plants, the concentration of As in the leaves can reach values between 1.0 and 1.7 mg kg<sup>-1</sup> (Kabata-Pendias 2011). Under hydroponic conditions and a supply of As (100 µM), the species A. atacamensis reached an As concentration of 25 mg  $kg^{-1}$  in the leaves (Vromman et al. 2011). However, the concentrations of metals or metalloids in the leaves found in plants grown in soil are lower because the metals/metalloids can be adsorbed in the solid phase of the soil and its bioavailability is lower. Tapia et al. (2013a, b) found that in A. atacamensis and A. halimus cultivated in pots in As-rich soils, the As concentrations in the leaves reached 2.6 $\pm$ 0.7 and 5.6 $\pm$ 1.8 mg kg<sup>-1</sup>, respectively, under controlled cultivation conditions. Díaz et al. (2011) found As levels of  $6.3 \pm 0.7$  mg kg<sup>-1</sup> in A. atacamensis collected in soils of these arid areas. However, no data are available for the As concentrations in A. halimus and A. nummularia established in situ in arid areas with high levels of this metalloid. There are few studies on the absorption of metals and metalloids by plants under realistic or field conditions, as has been confirmed by other researchers in relation to phytoremediation strategies (Arshad et al. 2008; Ali et al. 2013). The in situ assays could support the establishment of certain plants as strategies to counteract the high As content in the soils of these arid ecosystems. The objective of this study was to evaluate the accumulation of As and the growth parameters of A. atacamensis, A. halimus, and A. nummularia established in situ in an arid area.

## Materials and methods

Establishing the Atriplex plant in situ

The assay was conducted on a plot in the ChiuChiu village ( $22^{\circ}20'54.43''S$  68°38'53.96''W; 2525 m a.s.l.) located in the Atacama Desert and 35 km from the city of Calama in Northern Chile (Fig. 1). The soils of this area are classified as Aridisols. The soil of the plot is of non-agricultural use and has a sandy texture, containing 0.81 % organic matter, 0.21 % nitrogen, 0.06 % phosphorus, and 7.9 g kg<sup>-1</sup> Fe oxides (Tapia et al. 2013a, b. Prior to the establishment of plants, the soil was irrigated with water available in the plot (pH 8.1, electrical

Fig. 1 Study area in the Atacama Desert where the village of ChiuChiu is located (Northern Chile)



conductivity [EC] 0.65 dS m<sup>-1</sup>, As 0.23 mg L<sup>-1</sup>) to reduce the initial high electrical conductivity (14.0  $\pm 3.4$  dS m<sup>-1</sup>), which was determined in situ in a 1:5 (V/V) extract. In addition, the species *Tessaria* absinthioides was collected from the soil of this plot because it was the dominant plant under the natural conditions. The shrubs A. atacamensis, A. halimus, and A. nummularia (average height of 42 cm) were acquired from the nursery of the Centre for Arid Zone Studies of the University of Chile. Nine plants of each species (27 plants in total) were transplanted to a depth of approximately 10 cm. The plants were distributed randomly in rows over an area of 14 m<sup>2</sup> and with a plant density of two plants per m<sup>2</sup>. The irrigation frequency was once every 7-10 days, with an approximate volume of 300 mL of tap water obtained from the plot for each plant. The plants were maintained from January 2012 to May 2012 without fertilizer application and under the climatic conditions provided in Table 1. In addition, at the end of the assay, samples of the agricultural soils and aerial parts of the native species were collected near the assay area to determine the As concentrations. The native species collected were A. atacamensis, Distichlis spicata, and Tessaria absinthioides, which are "tropical inner desertic scrubs," and Cortaderia atacamensis, Lycium humile, Schinus molle, and Daucus carota (aerial and edible parts). The water for maintaining this vegetation and crop carrot comes from the Loa River, which passes through the village of ChiuChiu. The water from this river has the following properties: pH 8.3, EC 2.8 dS m<sup>-1</sup>, and As  $0.184 \text{ mg L}^{-1}$ ; these values are similar to those reported by Romero et al. (2003).

## Soil analysis

To determine the total As in the soils, dry soil samples (0.500 g) were finely ground and digested with 4 mL of Milli-Q H<sub>2</sub>O, 6 mL of HNO<sub>3</sub>, and 4 mL of H<sub>2</sub>O<sub>2</sub> in an autoclave (Huxley Speedy HL-341, Sanchong District, Taiwan) at 125 °C for 35 min (Moreno et al. 2010). The extract was then filtered, and the As concentration was measured by flow injection hydride generation atomic absorption spectrophotometry (FI-HG-ASS) using a Thermo Electronic Corporation AA Series apparatus (Waltham, MA, USA) and a Perkin Elmer FIA 100 apparatus (detection limit 0.01  $\mu$ g As L<sup>-1</sup>) (Waltham, MA, USA). Sequential soil extraction of As was performed in randomly collected soils to evaluate the association of the metalloid with the different soil fractions. Sequential extraction was performed in soil samples at the beginning (without plants) and end of the assay (after of the cultivation of plants). The soil samples were distributed in five fractions, with four samples per fraction: non-specifically adsorbed (F1) extracted with  $(NH_4)_2SO_4$ , specifically adsorbed (F2) extracted with (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>, amorphous and poorly crystalline Fe and Al oxides (F3) extracted with NH<sub>4</sub> buffer oxalate, well-crystallized Fe and Al oxides (F4) extracted with NH<sub>4</sub> buffer oxalate and ascorbic acid, and residual (F5) digested with HNO<sub>3</sub> and  $H_2O_2$  (Wenzel et al. 2001). The As concentration in each step was determined by FI-

Month	Temperature (°C)		Relative humidit	Relative humidity (%)		Wind speed (km $h^{-1}$ )	
	Minime	Maxime	Minime	Maxime	Minime	Maxime	
January	$5.6 \pm 2.3$	$23.2 \pm 5.6$	$25.1 \pm 9.5$	$78.3\pm12.9$	$1.6 \pm 0.5$	$35.7 \pm 3.5$	
February	$7.7 \pm 3.2$	$22.5\pm0.9$	$35.1\pm10.9$	$82.9 \pm 10.0$	$1.0\pm0.7$	$32.2\pm3.7$	
March	$6.8 \pm 2.4$	$24.3\pm1.8$	$18.6 \pm 11.7$	$72.2 \pm 22.3$	$1.5 \pm 1.0$	$32.0\pm5.7$	
May	$3.3\pm2.6$	$22.7\pm1.8$	$10.1 \pm 2.0$	$42.2\pm18.8$	$2.0\pm1.1$	$28.0\pm4.2$	

Table 1 Climatic conditions during the assay in the ChiuChiu village located in the Atacama Desert, Northern Chile (means  $\pm$  standard deviations, n = 30)

HG-AAS. The electrical conductivity and pH of soils in situ and at the bottom of each established plant (n=27) were determined monthly using a multi-parameter instruments model HI 991301 (Hanna Instruments, RI. USA). Montana Soil SRM 2711 was employed to evaluate the accuracy of the As concentrations. The certified As concentration for this soil is As  $105\pm8 \ \mu g \ g^{-1}$ , and the value obtained was As  $98.19\pm0.03 \ \mu g \ g^{-1}$ . Deionized water (18 M $\Omega$  cm) was used to prepare the reagents and standards. All chemicals were of professional analysis quality, and a certified standard solution of As and metals was used (Merck, Darmstadt, Germany).

## Analysis of the plants

The As concentration and dry weight of the plants were determined for the aerial part (leaves+stem) and the roots at the beginning of the assay (day 0) and at the end of the assay (day 120). At days 60 and 90, the As concentration was determined for the leaves and stems. For this, the sampling of the aerial part was performed in a suitable amount (~1.0-g fresh weight) of plants visually not stressed. The plant height was measured monthly. For the plant analysis in the assay and the native plants collected in soils around the assay, samples were carefully washed with tap water and then with distilled water three times. The finely ground and dried (at 65 °C for 48 h) vegetable samples (0.500 g) were digested with 10 mL of Milli-Q H<sub>2</sub>O, 3 mL of HNO<sub>3</sub>, and 2 mL of  $H_2O_2$  in an autoclave at 125 °C and 1.5 kg cm<sup>2</sup> for 35 min (Moreno et al. 2012). The As concentration in the digested extract was determined by FI-HG-AAS. The As concentration is expressed in mg  $kg^{-1}$  of plant on a dry basis. The bioconcentration factor (BCF) was calculated as BCF=As concentration in the leaves/As concentration in soil, and the transport index (Ti) was calculated as Ti=As concentration in the leaves/As concentration in the roots (Ghosh and Singh 2005). The increase in the dry weight of the aerial part (%)=dry weight of the aerial part at the beginning of the assay/dry weight of the aerial part at the end of the assay × 100. Standard reference of vegetative material 1573a of the National Institute of Standards and Technology for As concentrations was employed to evaluate the accuracy of the results. The certified As concentration of this material is  $0.112\pm0.004$  mg kg<sup>-1</sup>, and the value obtained was  $0.106\pm0.03$  mg kg<sup>-1</sup>.

## Statistical analysis

The statistical analysis was based on a one-way analysis of variance (ANOVA) of the mean values of the concentration of As, BFC, Ti, dry weight, and height for *A. atacamensis*, *A. halimus*, and *A. nummularia* to test the statistically significant differences using the Duncan test at  $p \le 0.05$ . All of the statistical tests were conducted using the SPSS v 22.0 software package.

## Results

## Concentration and distribution of As in soil

The total As concentration in soil at the beginning of the assay was  $131.2 \pm 10.0 \text{ mg kg}^{-1}$  (Table 2). At the end of the assay, the total As concentration in the soil had decreased significantly to  $103.3 \pm 1.3 \text{ mg kg}^{-1}$ . These concentrations are higher than those found in agricultural soils around the assay of  $44.5 \pm 13.6$  (Table 3). Regarding the sequential extraction performed on the soil of the assay, As was found to be primarily associated with fraction III or to amorphous and poorly crystal-line Fe and Al oxides (Table 2). The As associated with

	As total	Arsenic (mg kg <sup>-1</sup> )					Sum	Recovery (%)
		FI	FII	FIII	FIV	FV		
Initial soil	$131.2 \pm 10.4a$	18.7±0.5a	$30.9 \pm 1.4a$	38.0±1.1a	$3.5\pm0.3a$	9.2±2.9a	110.3	84
To end soil	$103.3\pm11.3b$	$20.1\pm0.7a$	$31.8\pm0.6a$	$39.1\pm0.6a$	$3.3\pm0.5a$	$16.5\pm1.4a$	110.9	107

**Table 2** Arsenic total (mg kg<sup>-1</sup>) and sequential extraction in the soil and at the beginning and end of the assay performed in the village of ChiuChiu, Northern Chile (means  $\pm$  standard deviations, n = 4)

Different letters in rows indicate significant differences among the species according to the Duncan test at  $p \le 0.05$ 

fractions FI+FII was 49.6 mg kg<sup>-1</sup>, i.e., the metalloid showed high availability in this soil (38 %). At the end of the assay, the As distribution in different soil fractions did not differ from the initial soil of the assay.

#### Measurement of the salinity and pH of the soil in situ

The electrical conductivity of the soil determined in situ in the plot showed high variability, with values between 4.10 and 9.90 dS m<sup>-1</sup> (1:5 V/V extract). The pH of the soil was alkaline, with an average value of 8.6 (Table 4).

## Growth parameters of the plants

After transplanting the cuttings of *Atriplex* in the soils, the survival rates were 44 % for *A. atacamensis* and *A. halimus* and 78 % for *A. nummularia*. Then, four

**Table 3** Arsenic concentration (mg kg<sup>-1</sup>) in agricultural soils and in native plants collected around the assay in the village of ChiuChiu, Northern Chile (means  $\pm$  standard deviations, n = 4)

Plant species	Arsenic in agricultural soils (mg kg <sup>-1</sup> )	Arsenic in plant (mg kg <sup>-1</sup> )
Atriplex atacamensis (leaves)	$35.5\pm14.0$	$3.42 \pm 0.73$
Distichlis spicata (leaves)	$35.5\pm14.0$	$3.61\pm0.88$
Tessaria absinthioides (leaves)	$131.2 \pm 10.4^{a}$	$5.10 \pm 0.70$
-	$35.5\pm14.0$	$3.82\pm0.53$
Lycium humile (leaves)	$45.0\pm\!6.8$	$2.55\pm0.73$
Cortaderia atacamensis (stem)	$78.0 \pm 13.6$	$1.61 \pm 0.42$
Cortaderia atacamensis (flowers)	$78.0\pm13.6$	$2.98\pm0.84$
Daucus carota (edible part)	$37.9 \pm 10.6$	$0.75\pm0.13$
Daucus carota (leaves)	$37.9 \pm 10.6$	$3.64\pm0.61$
Schinus molle (leaves)	$50.7\pm\!2.50$	$3.60 \pm 0.84$

<sup>a</sup> Soil of non-agricultural use

plants of each species were evaluated in the assay. The height and dry weight of *A. atacamensis*, *A. halimus*, and *A. nummularia* increased each month (Table 5). At the end of the assay, the increase in dry weight of the aerial part of *A. nummularia* and *A. halimus* was approximately 30 % greater than that for *A. atacamensis* (Fig. 2).

### Concentration of As in the plants

At the beginning of the assay, the plants exhibited an As concentration of approximately 1.0 mg kg<sup>-1</sup>, which is a level commonly found in plants (Kabata-Pendias 2011). At day 60, the As concentration in the leaves was significantly higher in *A. halimus* than that in *A. atacamensis* and *A. nummularia* (Table 6). At day 90, the As concentration in the leaves in *A. atacamensis* was lower than that in the other plants of *Atriplex*. At the end of the assay, the As concentration in the leaves, stems, and roots of *A. halimus* was higher than that in *A. atacamensis* and *A. nummularia*, but the difference was not significant. The three species accumulated significantly higher As levels in the roots. The BCF of As

**Table 4** pH and electrical conductivity (dS m<sup>-1</sup>) measured in situ in the soil (1:5 (V/V) extract) in the village of ChiuChiu, Northern Chile (means ± standard deviations, n = 27)

Month	Soil in situ 1:5 $(V/V)$ extract			
	рН	Electrical conductivity (dS $m^{-1}$ )		
January	$8.5 \pm 0.5$	$5.49 \pm 1.87$		
February	$8.5 \pm 0.1$	$4.10 \pm 1.36$		
March	$8.6 \pm 0.1$	$6.96 \pm 2.05$		
April	$8.6 \pm 0.1$	$9.90 \pm 3.41$		
May	$8.7 \pm 0.1$	$8.86 \pm 2.97$		
Average	$8.6 \pm 0.1$	$7.06 \pm 2.37$		

Days	Parameters	Organs	A. atacamensis	A. halimus	A. nummularia
0	Dry weight (g)	Aerial part	$1.5 \pm 0.4$	$2.2 \pm 0.5$	$2.1 \pm 0.6$
		Root	$1.14 \pm 0.1$	$0.73\pm0.1$	$0.60 \pm 0.1$
	Hight (cm)	_	$44.3 \pm 2.5$	$47.3 \pm 6.9$	$39.2 \pm 5.4$
30	Hight (cm)	Aerial part	$45.0 \pm 2.7$	$48.3 \pm 6.9$	$40.2\pm5.4$
60	Hight (cm)	Aerial part	$45.9 \pm 3.1$	$52.3 \pm 7.8$	$42.8\pm5.4$
90	Hight (cm)	Aerial part	$48.1 \pm 6.5$	$57.3 \pm 7.9$	$47.5\pm7.6$
120	Dry weight (g)	Leaves	$5.3 \pm 1.7$	$8.5 \pm 2.1$	$13.0 \pm 2.9$
		Stem	$3.5\pm0.1$	$13.7 \pm 1.9$	$7.0\pm0.5$
		Root	$1.3 \pm 0.3$	$4.5\pm0.6$	$5.7\pm0.4$
	Hight (cm)	Aerial part	$48.5\pm6.0$	$55.3\pm\!4.6$	$47.8\pm5.3$

**Table 5** Dry weight (g) and height (cm) of *A. atacamensis*, *A. halimus*, and *A. nummularia* measured during the assay (means  $\pm$  standard deviations, n = 4)

generally increased with time in the assays for the three species (Fig. 3). However, *A. halimus* exhibited a higher As accumulation factor at the end of the assay. The transport index to the leaf was less than 1 in the three species without significant differences at the end of the assay (Fig. 4).

With respect to the native plants collected from agricultural soils around the assay, the plants that form "tropical inner desertic scrubs" exhibited an As concentration of 3.42 to  $3.82 \text{ mg kg}^{-1}$ , whereas the other native plants exhibited an As concentration of 1.61 to 3.60 mg kg<sup>-1</sup> (Table 3). However, *T. absinthioides* that was collected in the soil of the assay exhibited a higher As level of 5.10 mg kg<sup>-1</sup>. The As concentration in



Fig. 2 Increases in the dry weight of the aerial part (g) after 120 days (*lines in bars* correspond to the standard deviation, n=4; *different letters above the bars* indicate significant differences among the species according to the Duncan test at  $p \le 0.05$ )

*D. carota* was higher in the leaves than that in the edible portion.

## Discussion

The concentration of As in the soils of the assay was noticeably higher  $(131.2 \pm 10.4 \text{ mg kg}^{-1})$  than that in the soils collected from agricultural soils around the assay  $(44.5 \pm 13.6 \text{ mg kg}^{-1})$ . This higher concentration is

**Table 6** Arsenic concentration (mg kg<sup>-1</sup>) in *A. atacamensis*, *A. halimus*, and *A. nummularia* cultivated in soil with high levels of arsenic in the village of ChiuChiu, Northern Chile (means  $\pm$  standard deviations, n=4)

Organs	A. atacamensis	A. halimus As (mg kg <sup><math>-1</math></sup> )	A. nummularia
Aerial part	$1.39 \pm 0.45a$	$0.51 \pm 0.17b^*$	1.27±0.26ab*
Root	$2.40 \pm 1.06a$	$2.66 \pm 0.57 ab^{\ast}$	$3.92 \pm 0.69b^*$
Leaves	$2.56 \pm 1.38a$	$3.93 \pm 1.06 b$	$2.10 \pm 0.94a$
Leaves	$2.46 \pm 1.82a$	$4.53\pm1.14b^{\ast}$	$3.85\pm0.64b$
Stem	$2.39\pm0.90a$	$2.25 \pm 0.18a^*$	$2.49 \pm 1.44a$
Leaves	$3.53\pm0.76a$	$4.98 \pm 1.63a$	$4.22 \pm 0.59a^*$
Stem	$2.52 \pm 1.23a^*$	$3.87 \pm 1.47a^*$	$3.16 \pm 0.74a^*$
Root	$5.35 \pm 2.17a^*$	$6.54 \pm 0.49a^*$	$6.49 \pm 1.11a^*$
BF	_	_	_
Ti	_	_	-
	Organs Aerial part Root Leaves Stem Leaves Stem Root BF Ti	Organs A. atacamensis   Aerial $1.39 \pm 0.45a$ part $2.40 \pm 1.06a$ Root $2.40 \pm 1.38a$ Leaves $2.46 \pm 1.82a$ Stem $2.39 \pm 0.90a$ Leaves $3.53 \pm 0.76a$ Stem $2.52 \pm 1.23a^*$ Root $5.35 \pm 2.17a^*$ BF $-$ Ti $-$	Organs A. atacamensis A. halimus As (mg kg <sup>-1</sup> )   Aerial part 1.39±0.45a 0.51±0.17b*   Root 2.40±1.06a 2.66±0.57ab*   Leaves 2.56±1.38a 3.93±1.06b   Leaves 2.46±1.82a 4.53±1.14b*   Stem 2.39±0.90a 2.25±0.18a*   Leaves 3.53±0.76a 4.98±1.63a   Stem 2.52±1.23a* 3.87±1.47a*   Root 5.35±2.17a* 6.54±0.49a*   BF - -   Ti - -

Different letters in rows indicate significant differences among the species of *Atriplex* according to the Duncan test at  $p \le 0.05$ . Asterisks in columns indicate significant differences among the organs according to the Duncan test at  $p \le 0.05$ 



Fig. 3 Bioaccumulation factor of arsenic ([As in the leaves/As in soil]) in the species of genus *Atriplex* (*lines in bars* correspond to the standard deviation, n = 4; *different letters above the bars* 

indicate significant differences among the species at days 0, 60, 90, and 120 of the assay according to the Duncan test at  $p \le 0.05$ )

likely due to a wash of As in agricultural soils from the continuous application of irrigation water. Therefore, the concentration of As in the village of ChiuChiu depends on the soil sampling location. Other authors in this village obtained As concentrations in soils of 17.2 mg kg<sup>-1</sup> (Pizarro et al. 2003), 53 mg kg<sup>-1</sup> (Díaz et al. 2011), and 111 mg kg<sup>-1</sup> (Tapia et al. 2013a, b).

Regarding the sequential extraction of As in the soils of this assay, the high bioavailability of this metalloid is attributed to the chemistry characteristics of these soils,



Fig. 4 Transport index of arsenic ([As in the leaves/As in the roots]) in the species of genus *Atriplex* (*lines in bars* correspond to the standard deviation, n = 4; *different letters above the bars* 

indicate significant differences among the species at days 0 and 120 of the assay according to the Duncan test at  $p \le 0.05$ )

namely, the alkaline pH and low content of both organic matter and Fe oxides, conditions under which the As is poorly retained (Moreno et al. 2012). Ascar et al. (2008) obtained a total As concentration of 59 mg  $kg^{-1}$  in the central zone of Chile, associated primarily with fraction III (42 %), i.e., the fraction of amorphous and poorly crystalline Fe and Al oxides. These soils exhibited a pH of 6.6, an organic matter content of 3.2 %, and an iron oxide content of 24.3 g kg<sup>-1</sup>, in contrast to the soils of this study, which had a higher pH (pH 8.4), lower organic matter content (0.81 %), and lower Fe oxide content (7.9 g kg<sup>-1</sup>). These conditions favor the association of As with more available fractions in this soil, such as FI+FII (49.6 mg kg<sup>-1</sup>, 38 % of total As). The As in soil of this assay was also predominantly associated with fraction III of the amorphous and poorly crystalline Fe and Al oxides, indicating the high affinity of Fe oxides to form complexes with As. There are numerous investigations related to Fe oxides as potential amendments to immobilize As (Fitz and Wenzel 2002; Visoottiviseth et al. 2002; Litter et al. 2010; Komárek et al. 2013). The trace metals/metalloids in the soil are preferentially associated with the fractions associated with Fe and Mn oxides and to the residual fraction, depending on the soil properties, that are fractions of lower availability for the plants (Alloway 2010; Adriano 2001).

The high pH and electrical conductivity values determined in situ in these soils are characteristic of arid areas, in which rainfall is scarce, and thus, salt accumulation occurs. The pH is relatively stable; however, the electrical conductivity exhibits high variability. This variability may be due to the capillary rise of the moisture, which draws salts to the surface in an irregular form (Brady and Weil 2002), and the salt transport by wind, which is permanent and characteristic of this arid area. The electrical conductivity values are high, considering that the values were obtained in a 1:5 (V/V) soil extract. Excess salinity is a major constraint to the development of plants. However, plants of the genus Atriplex are halophytes, and some authors have reported that they can tolerate soils with an electrical conductivity of 10-12 dS m<sup>-1</sup> in the saturated soil extract (Manousaki and Kalogerakis 2009). In the present study, the Atriplex plants tolerated an electrical conductivity of 10 dS m<sup>-1</sup>, determined in a 1:5 (V/V) soil extract, without reducing their growth parameters during the assay. However, A. atacamensis grew more slowly than A. nummularia and A. halimus.

Regarding the generation of biomass, studies using the genus *Atriplex* as fodder plants have shown that *A. nummularia* and *A. halimus* generate biomass rapidly (Abu-Zanata et al. 2004), and their growth is stimulated in the presence of salts (Gomes et al. 2008; Manousaki and Kalogerakis 2011; Nedjimi 2014). In another assay with *A. halimus* in the presence of As, this species also showed a higher biomass compared to *A. atacamensis* (Tapia et al. 2013a, b). Biomass generation is an important aspect when the plants are evaluated for phytostabilization strategies (Santibáñez et al. 2008). The high biomass generation can be used to compensate for the low accumulation of metals and metalloids of the common plants (Zhuang et al. 2007; Hernández-Allica et al. 2008).

The As concentration in the three species of *Atriplex* established in situ exceeds the level commonly found in plants. The As level required to cause phytotoxicity in most plants ranges from 3 to  $10 \text{ mg kg}^{-1}$  (Madejon et al. 2002). In woody plants grown in soils with high levels of As (52–218 mg kg<sup>-1</sup>), As concentrations of 0.27 to 2.29 mg  $kg^{-1}$  have been found in the aerial part (Madejón and Lepp 2007). Most plants tend to accumulate metals more in the roots than in the leaves (Moreno et al. 2012). However, plants of the genus Atriplex, especially A. nummularia and A. halimus, tend to transport the As to the aerial parts due to their halophytic character (Manousaki and Kalogerakis 2011). Transport to the aerial part after 60 days is more rapid in A. halimus compared to the other two species. This feature of A. halimus has been observed for As in a pot assay (Tapia et al. 2013a, b) as well as for cadmium (Tapia et al. 2011) and lead (Tapia et al. 2013b). A. nummularia and A. halimus not decreases in their growth parameters with increasing concentrations of As. For these two species, the As concentration in the leaves at the end of the assay was higher than in native plants collected from soils around the assay. In contrast, for A. atacamensis, the As levels in the leaves were similar to the levels found in the same species collected from soils around the assay. A. atacamensis is a plant native of this area, which has high levels of As; therefore, the plant has likely developed certain adaptive mechanisms that control the transport of the metalloid to the aerial part.

The As levels in the leaves of *A. atacamensis* and *A. halimus* obtained in situ in this assay (3.53 and 4.98 mg kg<sup>-1</sup>, respectively) are comparable to those obtained in an assay in which these plants were

cultivated in pots under controlled conditions (2.57 and 5.59 mg kg<sup>-1</sup>, respectively) (Tapia et al. 2013a, b). These results indicate that these plants maintain their ability to tolerate As regardless of whether they are established in field conditions. However, the As levels in plants are not high despite the high concentrations of As available in these soils. The species *A. halimus* accumulated approximately 10 % of the As available considering that this fraction is 49.6 mg kg<sup>-1</sup>.

In plants that form "tropical inner desertic scrubs" collected in agricultural soils around the assay, the As concentration also exceeded the common levels found in plants. The As concentrations of 3.4 to 3.6 mg kg<sup>-1</sup> found in the leaves of desert scrubs, in the native tree Schinus molle, and in the leaves of Daucus carota can be considered reference data for native plants in this zone, which has been identified as having a high exposure to As. The As concentration found in the edible part of the carrot (0.75 mg kg<sup>-1</sup> dw) is comparable to those obtained by other authors in the same village  $(0.36 \text{ mg kg}^{-1} \text{ ww})$  (Muñoz et al. 2002) and does not exceed the levels permitted for food in the Chilean legislation (1 mg kg<sup>-1</sup> dw; RSA 1997). However, extremely high concentrations in the edible part of the carrot (49 mg kg<sup>-1</sup>) have been found by Pizarro et al. (2003) in the same village of ChiuChiu in soil with an As concentration of 17 mg kg<sup>-1</sup>. This result could be attributed to the water irrigation of the Loa River; however, the authors did not provide data on the As concentration of the irrigation water.

The rising BCF of As with increasing biomass is a positive behavior in the three species of Atriplex if the strategy is to mitigate the high concentrations of the metalloid in the soils and create vegetative cover. When the BCF is greater than 1, the phytoextraction of any element is feasible (McGrath and Zhao 2003). However, the three species showed low values of BCF. Other assays found that A. halimus showed a higher BCF of As compared with A. atacamensis (Tapia et al. 2013a, b). In assays related to cadmium phytoextraction, A. halimus also showed a higher BCF than other species (Tapia et al. 2011). With respect to index of transport, the levels of As in the three species were higher in the roots than those in the leaves; therefore, the dominant mechanism was phytostabilization of As. This result has also been recently reported for A. halimus (Pérez-Esteban et al. 2013). The tendency of A. halimus to accumulate metals and its rapid generation of biomass justify recommending this species as vegetative cover for soils that have been developed for mining activities (Lutts et al. 2004; Walker et al. 2014). Other authors also found that *A. halimus* has a higher accumulation capacity for ions than *A. nummularia* and has been related to proline synthesis (Belkheiri and Mulas 2013).

The phytostabilization of metals and metalloids is an appropriate strategy for arid ecosystems. It is difficult to generate biomass in these environments due to the lack of water and high salinity; hence, phytostabilization is more convenient because the plant remains intact and accumulates As in the root. Furthermore, the biomass generation prevents the transport of this metalloid by wind.

## Conclusions

The As concentrations in the soils of the village of ChiuChiu depend on the soil sampling location. In soils of non-agricultural use, the total As concentration was  $131.2 \pm 10.0 \text{ mg kg}^{-1}$ . The As in these soils was found in highly available fractions, which is attributed to the alkaline pH, low organic matter and iron oxide content, and sandy texture. A. halimus and A. nummularia established in situ exhibited an approximately 30 % higher dry weight of the aerial part than A. atacamensis. The levels of As in the aerial part in the three species of genus Atriplex ranged from 3.53 to 4.98 mg kg<sup>-1</sup>, whereas the levels of As found in plants that grow naturally in the zone ranged from 3.4 to 3.6 mg  $kg^{-1}$ . The three species of Atriplex established in situ were shown to have a phytostabilization capacity of As. This plants can be used to remediate soils with high levels of this metalloid in areas in which it is difficult to establish plants, such as in arid regions and under salty conditions.

Acknowledgments This work was supported by the National Commission for Scientific and Technological Research (CONICYT) of the Ministry of Education, Chile, Project FONDECYT 3110001 and 1150513. Authors are grateful to Rafael Arcos and Kimberly Saire for his collaboration in this project.

#### References

- Abu-Zanata, M. W., et al. (2004). Increasing range production from fodder shrubs in low rainfall areas. *Journal of Arid Environments*, 59, 205–216.
- Adriano, D. C. (2001). Trace elements in terrestrial environments (2nd ed.). New York: Springer. 867 p.

- Akhani, H., et al. (1997). Photosynthetic pathways in Chenopodiaceae from Africa, Asia and Europe with their ecological, phytogeographical and taxonomical importance. *Plant Systematics and Evolution*, 206, 187–221.
- Ali, H., et al. (2013). Phytoremediation of heavy metals—concepts and applications. *Chemosphere*, 91, 869–881.
- Alloway, B. (2010). Heavy metals in soil. Trace metals and metalloids in soil and their bioavailability. New York: Springer. 613 p.
- Arshad, M., et al. (2008). A field study of lead phytoextraction by various scented Pelargonium cultivars. *Chemosphere*, 71, 2187–2192.
- Ascar, L., et al. (2008). Effect of biosolid incorporation on arsenic distribution in Mollisol soils in central Chile. *Chemosphere*, 70, 1211–1217.
- Belkheiri, O., & Mulas, M. (2013). The effects of salt stress on growth, water relations and ion accumulation in two halophyte Atriplex species. *Environmental and Experimental Botany*, 86, 17–28.
- Brady, N. C., & Weil, R. (2002). *The nature and properties of soils* (13th ed.). New Jersey: Prentice Hall. 975 p.
- Bundschuh, J., et al. (2012). Arsenic in the human food chain: the Latin American perspective. Science of the Total Environment, 429, 92–106.
- Cáceres, L., et al. (1992). Water recycling in arid regions. Chilean case. Ambio, 21, 138–144.
- Clemente, R., et al. (2012). The use of a halophytic plant species and organic amendments for the remediation of a trace elements-contaminated soil under semi-arid conditions. *Journal of Hazardous Materials*, 223–224, 63–71.
- Díaz, O., et al. (2011). Total and bioavailable arsenic concentration in arid soils and its uptake by native plants from the Pre-Andean zones in Chile. *Bulletin of Environmental Contamination and Toxicology*, 666–669.
- Figueroa, J., et al. (2004). Exotic plant invasion to the Mediterranean region of Chile: causes, history and impacts. *Revista Chilena de Historia Natural*, 77, 465–483.
- Fitz, W. J., & Wenzel, W. (2002). Arsenic transformations in the soil–rhizosphere–plant system: fundamentals and potential application to phytoremediation. *Journal of Biotechnology*, 9, 259–78.
- Ghosh, M., & Singh, S. P. (2005). A comparative study of cadmium phytoextraction by accumulator and weed species. *Environmental Pollution*, 133, 365–371.
- Gomes, I., et al. (2008). Fitorremediação de solo salino sódico por Atriplex nummularia e gesso de Jazida. Revista Brasileira de Ciência do Solo, 32, 1065–1072.
- Hernández-Allica, J., et al. (2008). Assessment of the phytoextraction potential of high biomass crop plants. *Environmental Pollution*, *152*, 32–40.
- Kabata-Pendias, A. (2011). Trace elements in soil and plants. 4th Edition (520 p). CRC Press NY.
- Komárek, M., et al. (2013). Chemical stabilization of metals and arsenic in contaminated soils using oxides. A review. *Environmental Pollution*, 172, 9–22.
- Lailhacar, S., & Torres, C. (2001). Influencia de los arbustos del género Atriplex L. con y sin corte de rebaje en el comportamiento del estrato herbáceo del secano arido. 1. Efecto del arbusto promedio del género sobre las características cuantitativas del estrato herbáceo total. Avances Producción Animal, 26, 79–96.

- Lailhacar, S., et al. (1991). Soil variables to be considered when selecting soils for plantation of the shrub Atriplex nummularia Lindl. Avances Producción Animal, 16, 47–66.
- Lailhacar, S., et al. (1995). Rendimiento de leña y recuperación al corte en diferentes especies y procedencias arbustivas del género Atriplex. Revista de Ciencias Forestales, 10(1–2), 85–97.
- Latorre, C., et al. (2006). Late quaternary vegetation and climate history of a perennial river canyon in the Río Salado basin (22°S) of northern Chile. *Quaternary Research*, 65, 450– 466.
- Le Houérou, H. N. (1992). The role of saltbushes (*Atriplex* spp.) in arid land rehabilitation in the Mediterranean basin: a review. *Agroforestry Systems*, 18, 107–148.
- Litter, M., et al. (2010). Possible treatments for arsenic removal in Latin American waters for human consumption. *Environmental Pollution*, 158, 1105–1118.
- Luebert, F., & Pliscoff, P. (2006). Sinposis bioclimática y vegetacional de Chile (316 p.) Universitaria, Chile.
- Lutts, S., et al. (2004). Heavy metal accumulation by halophyte species Mediterranean saltbush. *Journal of Environmental Quality*, 33, 1271–1279.
- Madejon, P., et al. (2002). Bioaccumulation of As, Cd, Cu, Fe and Pb in wild grasses affected by the Aznalcollar mine spill (SW Spain). Science of the Total Environment, 290, 105–120.
- Madejón, P., & Lepp N. W. (2007). Arsenic in soils and plants of woodland regenerated on an arsenic-contaminated substrate: a sustainable natural remediation? *Science of Total Environmental*, 379, 256–262.
- Manousaki, E., & Kalogerakis, N. (2009). Phytoextraction of Pb and Cd by the Mediterranean saltbush (*Atriplex halimus* L.): metal uptake in relation to salinity. *Environmental Science* and Pollution Research, 16, 844–854.
- Manousaki, E., & Kalogerakis, N. (2011). Halophytes—an emerging trend in phytoremediation. *International Journal of Phytoremediation*, 13, 959–969.
- McGrath, S. P., & Zhao, F. J. (2003). Phytoextraction of metals and metalloids from contaminated soils. *Current Opinion in Biotechnology*, 14, 277–282.
- Mendez, M., et al. (2007). Phytostabilization potential of quailbush for mine tailings: growth, metal accumulation, and microbial community changes. *Journal of Environmental Quality*, 36, 245–253.
- Moreno-Jiménez, E., et al. (2010). Hydroponics as valid tool to assess arsenic availability in mine soils. *Chemosphere*, 79, 513–7.
- Moreno-Jiménez, E., et al. (2012). The fate of arsenic in the soilplant system. *Reviews Environmental Contamination and Toxicology*, 215, 1–37.
- Muñoz, O., et al. (2002). Vegetables collected in the cultivated Andea Area of Northern Chile: total and inorganic arsenic contents in raw vegetables. *Journal of Agricultural and Food Chemistry*, 50, 642–647.
- Nedjimi, B. (2014). Effects of salinity on growth, membrane permeability and root hydraulic conductivity in three saltbush species. *Biochemical Systematics and Ecology*, 52, 4–13.
- Pérez-Esteban, J., et al. (2013). Bioavailability and extraction of heavy metals from contaminated soil by *Atriplex halimus*. *Environmental and Experimental Botany*, 88, 53–59.
- Pizarro, I., et al. (2003). Distribution of arsenic species in environmental samples collected in Northern Chile. *International*

Journal of Environmental Analytical Chemistry, 83, 879–890.

- Poblete, V., et al. (1991). Anatomical leaf adaptations in vascular plants of salt marsh in the Atacama Desert (Chile). *Revista Chilena de Historia Natural*, 64, 65–75.
- Queirolo, F., et al. (2000). Total arsenic, lead, and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. Science of theTotal Environment, 255, 75–84.
- Riedemann, P., et al. (2006). Flora nativa de valor ornamental. Identificación y propagación. Chile zona Norte (404 p). Riedemann, Aldunate, Teillier. Chile.
- Romero, L., et al. (2003). Arsenic enrichment in waters and sediments of the Rio Loa (Second Region, Chile). *Applied Geochemistry*, 18, 1399–416.
- RSA (1997). Reglamento Sanitario de los Alimentos, Chile. D. Oficial de la República de Chile 35764, 3–32.
- Saiz, F., et al. (2000). Biodiversidad de complejo de artrópodos asociados al follaje de la vegetación del norte de Chile, II Región. *Revista Chilena de Historia Natural*, 73, 671–692.
- Sánchez, A., & Morales, R. (2004). Las Regiones de Chile. Cuarta edición (152 p). Universitaria. Chile.
- Santibáñez, C., et al. (2008). Phytostabilization of copper mine tailings with biosolids: implications for metal uptake and productivity of Lolium perenne. *Science of the Total Environment*, 395, 1–10.

- Tapia, Y., et al. (2011). Phytoextraction of cadmium by four Mediterranean shrubs species. *International Journal of Phytoremediation*, 13, 567–579.
- Tapia, Y., et al. (2013a). Atriplex atacamensis and Atriplex halimus resist as contamination in Pre-Andean soils (northern Chile). Science of the Total Environmental, 450–451, 188–196.
- Tapia, Y., et al. (2013b). Effect of citric acid on metals mobility in pruning wastes and biosolids compost and metals uptake in *Atriplex halimus* and *Rosmarinus officinalis. Environmental Monitoring and Assessment, 185*, 4221–4229.
- Visoottiviseth, P., et al. (2002). The potential of Thai indigenous plant species for the phytoremediation of arsenic contaminated land. *Environmental Pollution*, 118, 453–461.
- Vromman, D., et al. (2011). Arsenic accumulation and distribution in relation to young seedling growth in *Atriplex atacamensis* Phil. *Science of the Total Environmental*, 412–413, 286–95.
- Walker, D. J., et al. (2014). Atriplex halimus L.: its biology and uses. Journal of Arid Environments, 100–101, 111–121.
- Wenzel, W., et al. (2001). Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta*, 436, 309–323.
- Zhuang, P., et al. (2007). Phytoextraction of heavy metals by eight plant species in the field. *Water, Air, & Soil Pollution, 184*, 235–242.