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MOBILITY OF ARSENIC IN *Allium sativum, Beta vulgaris* AND *Daucus carota* CROPS AT THE QUEBRADA DE CAMIÑA, NORTHERN CHILE

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ABSTRACT

The ravine Quebrada de Camiña, in northern Chile, is valued for regional agriculture, however, it retains high levels of As. From four locations (Chapiquilta, Camiña, Moquella, and Francia), environmental factors that affect the mobility of As were evaluated through the characterization of water quality and soil physicochemistry used for local crops of white garlic, beetroots and carrots; Contamination Factors, Geoaccumulation Index (CF-I_{GEO}), and operational speciation by BCR protocol in soils; Bioaccumulation Factors (BAF) and Translocation Factors (TF) for root-stem-bulb-leaves of Camiña white garlic plants, and BAF in beetroots and carrots. The results showed that water used in crops are slightly alkaline, mineralized with B and Na^+-Ca^{2+}/Cl^--SO_4^{2-}, that mobilize As (0.49 ± 0.02 mg/l) to the soils and are part of the fraction available and assimilable by the vegetables. The CF-I_{GEO} of saline soils showed low easily oxidized organic carbon, neutral pH and high levels of B, with moderate to considerable degree of total As contamination (123 ± 34 mg/kg); in fact, after soil As extraction protocol, 19% of As is found in the more available fractions and 79% in the residual phase, while a positive correlation with total As was observed. White garlic plants bioaccumulate As in roots (177 ± 18 mg/kg) and stems (81.0 ± 8.1 mg/kg), while the edible bulb (0.451 ± 0.054 mg/kg) and the leaves (0.073 ± 0.025 mg/kg) do not present a consumption risk. As translocations from root to stem and from bulb to leaves are observed. As in freeze-dried samples of beetroot (4.45 ± 0.98 mg/kg) and carrot (3.26 ± 3.50 mg/kg) showed fluctuation, exceeding national and international food standards.

Keywords: *arsenic, availability, bioaccumulation factor, translocation, vegetables.*

INTRODUCTION

Arsenic (As) is distributed in high concentrations in environmental matrices of several countries in Asia, Europe, North America, and South America [1,2]. In northern Chile, subjected to an extremely arid climate, As in natural waters essentially originates from the alteration of volcanic rocks and pyroclastic deposits; from the dissolution of As minerals in ignimbrite rocks; from the geothermal conditions of the Central Andes, as well as from the geological characteristics of each region [3 - 7] and also from the activities of mega-copper mining [8, 9].

The long-term use of irrigation water with high levels of As can increase its content in crop soils and plants, which is relevant in volcanic territories [4] and poses an environmental hazard due to availability for biota [10]. Several authors have demonstrated that the physicochemical properties of soils, such as acidity, microbial abundance, organic matter, nutrients, phosphates, As speciation, and substances from root exudates, effectively regulate the absorption and accumulation of As in different parts of plants [11 - 13]. The distribution among components and the mobility of As in soils depend on the climate, water infiltrations, and geomorphological conditions [14] and are also controlled by the parent material and irrigation practices [15]. There are specific mechanisms responsible for the mobility of chemical species in natural soils, characterized by oxidizing conditions. Currently, researchers use operational speciation to interpret the mobility of As from the solid matrix [16]. Caporale et al. [4], differentiated between non-specifically sorbed As and sorbed As in a study on its mobility in carrot plants. In the 1990s, the BCR (Community Bureau of Reference) implemented a standard protocol to improve and harmonize the speciation of trace elements, allowing for comparison with other researchers. The method considers four stages and four fractions: exchangeable, reducible, oxidizable, and residual fractions [10, 17, 18].

The most common route of As incorporation in humans is through drinking water and consumption of food and vegetables, posing a risk of cancer in exposed individuals [7]. Given that the root biomass is often more affected by contamination, there is concern about the accumulation of As in nutritious plants, such as tubers, whose edible portion is the main root, and the great benefits from the bioactive substances in carrots, beetroots, onions, and leafy vegetables such as lettuce, spinach, chili, and cucumber [4, 9, 11, 19 - 21].

In Chile, a recent investigation of the As levels in commonly consumed vegetables (Swiss chard, lettuce, spinach, and tomato) shows concentrations in the range of 0.14 to 0.31 mg/kg and suggests that prolonged exposure to an average of 0.20 mg/kg of As may pose a cancer risk and that the level of the metalloid in vegetables should be regulated [21]. In the Camiña Valley, northern Chile, as shown by Herrera et al. [22], there are high levels of As in irrigation water, soils, and in the roots of white corn plants (*Zea mays* L.), resulting in an excellent phytoremediator because As tends to accumulate in the roots, preventing high concentrations of As in the grain. However, there is no information available on other economically important crops, such as the highly sought-after bulb-stem vegetable known as Camiña white garlic (*Allium sativum*) and root vegetables like beetroot (*Beta vulgaris*) and carrot (*Daucus carota*).

The objective of the present study was to evaluate in plots from four locations (Chapiquilta, Camiña, Moquella, and Francia) in the Camiña ravine the environmental factors affecting the mobility of As through the characterization of irrigation water quality and soil physicochemistry; the contamination factor, geoaccumulation index and operational speciation by BCR protocol in soils; the bioaccumulation and translocation factors between root-stem-bulb-leaves of white garlic plants; and the bioaccumulation factors in beetroots and carrots to establish and communicate the potential food consumption risks.

EXPERIMENTAL PROCEDURE

The Tarapacá region, in northern Chile, is one of the arid zones of the world; however, there are various ravines-oriented East to West, between the Western Cordillera and the Pre-cordillera, which have surface and underground watercourses. To the north of the region, adjacent to the Camarones River basin, lies the exorreic basin of the Camiña River, whose hydrography has a permanent regime in the upper part, with numerous springs or water sources that feed it along the ravine. For its part, the basin exposes a varied lithological set, in which powerful tertiary sedimentary sequences stand out, housing the main aquifer of the area. Background from the monitoring network of the Dirección General de Aguas del Ministerio de Obras Públicas de Chile (DGA-MOP) reveals that average temperatures reach 20°C during the day, fluctuating between 5° and 8°C at night; an average precipitation value between 61 and 87 mm/year in the summer season, which favors recharge and runoff; and an average flow rate between 55 to 350 l/s, also indicating that in some places it infiltrates and reappears in the course of the ravine. However, the average evaporation is 80 mm/year [23]. In the basin of the Quebrada and due to agroclimatic characteristics, in the commune (administrative division of territorial policy) of Camiña, Province of Tamarugal, there are eleven localities at an average altitude of 1,700 to 3,200 meters above sea level (masl) and its communal capital of the same name at 2,314 masl, with terraced crops intended for the production of vegetables and greens and, to a lesser extent, family-level livestock farming.

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The towns are located on a level of river terraces higher than the main riverbed, except for Camiña, which is situated at a lower level and extends into the valley.

The study area corresponds to the localities of Chapiquilta (2,460 masl), Camiña (2,350 masl), Moquella (1,900 masl), and Francia (1,760 masl). Prior to the summer rains, field campaigns were carried out in December 2019. Duplicate samples of river water were collected from each locality; soil and garlic plant samples were taken from three small agricultural plots in Camiña (PC1, PC2, and PC3) and two in Francia (PF1 and PF2); soil and beetroot plant samples were collected from one agricultural plot in Moquella (PM2); soil and carrot plant samples were taken from two agricultural plots in Chapiquilta (PCh1 and PCh2) and one in Moquella (PM3); and soil samples were collected from one agricultural plot in Moquella (PM1). The coordinates for the sites of each plot and in the locality, according to symbols, are shown in table a.

Table a. Coordinates and identification of plots for the four locations in Quebrada de Camiña.

Locality	Plot	Latitude	Longitude
Chapiquilta	PCh1	19° 18’ 48,0’’ S	69° 24’ 49,9’’ W
	PCh2	19° 18’ 51,3’’ S	69° 24’ 54,8’’ W
Camiña	PC1	19° 18’ 41,2’’ S	69° 25’ 27,0’’ W
	PC2	19° 18’ 41,2’’ S	69° 25’ 43,0’’ W
	PC3	19° 18’ 42,2’’ S	69° 25’ 54,5’’ W
Moquella	PM1	19° 21’ 19,8’’ S	69° 31’ 30,5’’ W
	PM2	19° 21’ 20,9’’ S	69° 31’ 30,8’’ W
	PM3	19° 21’ 18,9’’ S	69° 31’ 34,6’’ W
Francia	PF1	19° 22’ 52,4’’ S	69° 34’ 21,6’’ W
	PF2	19° 22’ 59,5’’ S	69° 34’ 34,8’’ W

In the four locations, the temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), and redox potential (ROP) were measured in the river using HANNA HI9829 multiparametric equipment. The water samples were placed in containers with appropriate preservatives, filtered to 0.45 µm with a membrane filter, and the analyses were performed in duplicate following standardized protocols [24]. For the validation and interpretation of the results obtained from the chemical analysis of the major ions (Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, SO_4^{-2}, HCO_3^-, and CO_3^{2-}), samples with an ionic balance error of less than ± 10% have been considered [25].

From each of the plots, soil samples (n = 20) were taken between 0 and 20 cm in the form of pedons, 2-3 kg, and transported in airtight bags. They were dried at room temperature (22 ± 2 ºC), sieved to 2 mm, and stored in a desiccator. The moisture content was determined using the gravimetric method at 105 °C. The pH and electrical conductivity (EC) measurements were performed in 1:5 aqueous extracts using Hanna HI 9126 and Orion 3 Start Conductivity Benchtop desktop instruments, respectively. The determination of easily oxidizable organic carbon was performed by redox volumetry with potassium dichromate and ferrous sulfate, previously standardized. The percentage of limestone ($CaCO_3$) was determined by potentiometric titration with NaOH. For the quantification of nitrate ($N\text{-}NO_3^-$) in KCl extract, phosphate ($P\text{-}PO_4^{3-}$) by the Olssen method, and boron (B) in $CaCl_2$ extract by azomethine, the UV-Vis spectrophotometer Pekín Elmer Labda 25 [26] was used. For the digestion of the soil samples, the procedure suggested by Herrera et al. was followed [22], using Teflon bombs at 170 ± 5 °C with a 4:3:1 mixture of HCl, HNO_3, and HF sp, and H_3BO_3 PA. The sequential extraction protocol proposed by the BCR [17] considered the following, stage 1: a soil aliquot with 20 ml of 0.11 M acetic acid, stirred at 150 rpm for 16 h, and the residue was separated from the supernatant (exchangeable fraction); stage 2: the residue washed from the previous stage was treated with 20 ml of 0.1 M NH_2OHHCl adjusted to pH 2.0 (reducible fraction); stage 3: the residue from stage 2 was treated twice with 5 ml of 8.8 M H_2O_2 adjusted to pH 2.0 for 1 h, subsequently, digestion continued in a water bath at 85 °C for 1 h, 25 ml of 1 M NH_4OAc adjusted to pH 2.0 was added to the residue and stirred at 150 rpm for 16 h (oxidizable fraction); stage 4: the previous residue was transferred to the Teflon bomb and a mixture 3:1:2 of HCl, HNO_3, and HF were applied at 170 °C for 3 h; after cooling, H_3BO_3 was added. The extracts were kept in polyethylene containers and refrigerated before measurement.

For the collection of biological samples, complete specimens of Camiña white garlic, beetroot, and carrot plants were uprooted from the soil, shaken, washed with distilled water, and transported in organizer boxes to the laboratory. The separation of their main parts was carried out. The garlic plants had numerous fine roots; the stem was approximately 3 cm in diameter and 5 mm in height, in a plate shape; the bulb was composed of six to seven cloves in the axils, connected by the stem, wrapped in a leaf; and the inner and outer leaves ranged from 20 to 50 cm. The beetroot and carrot plants did not retain the main root appreciably; the parts for consumption, with reddish-purple and intense salmon colors, respectively, were reserved, and the leaves were discarded. The samples were washed with distilled water and air-dried for three days. They were reduced in size and left in a Gene Press Glacier Ultralow freezer at -86 °C; subsequently, they were lyophilized for 24 h in a Liotop L101 unit; they were pulverized with a plastic grinder and stored in a desiccator. For digestion, except for the garlic bulb, a 1:1 mixture of HNO_3 and $HClO_4$ sp was used at 80 °C for 2 h. For the digestion of bulb samples, various digestion tests were conducted, determining that the best method consisted of adding a 4:1 ratio of HNO_3 and H_2O_2 and heating at 20 °C for 18 h with regular agitation. An ideal digestion procedure for solid samples should be rapid, avoid losses of volatile elements and reduce contamination risks.

The determination of As was carried out by atomic absorption spectroscopy using the hydride generation mode on a Perkin Elmer model PinAAcle 900H/FIAS 100 after reducing from As (V) to As (III) with KI in an ascorbic acid and concentrated HCl medium; the analytical methodology was validated with certified reference materials of soil (San Joaquin Valley Soil SRM 2709/NIST) and tobacco (Virginia Tobacco Leaves CTA-VTL-2).

The Contamination Factor (CF) and the Geoaccumulation Index (I_{GEO}) in soils were determined considering a standard concentration of 20 mg/kg for soils in the Tarapacá region [22], similar to the baseline level of the Lhasa Basin in Tibet [16]. The Bioaccumulation Factor (BAF) between tissue and soil, and the Translocation Factor (TF) between plant parts were calculated based on total As in the matrices [12].

RESULTS AND DISCUSSION

Water quality

The results obtained *in situ* and the statistics of the physicochemical parameters of the waters, shown in table b, match very well with the data reported at the water quality monitoring station in Camiña by the DGA-MOP [23] and those from a previous study in Camiña [22]. Regarding the temperature, downstream waters are slightly warmer, considering that along the longitudinal axis of the channel there is a greater surface area exposed to solar radiation and there is less altitude. Redox conditions in the runoff exert control over the natural concentration of DO, with more oxygenated waters also observed in the sector of Francia. In the course of the shallow river, oxygen is constantly being replenished, which is demanded by reducing species, such as As(III). The ROP values were close to 0.0 mV, indicates stable redox conditions and groundwater origin [24]. The pH measurements indicate slightly alkaline waters, with a slight decrease in acidity in Chapiquilta. As is well known, the oxidation state of As, and therefore its mobility and toxicity, are controlled by ROP and pH. The geochemical classification by dry residue (TDS) and EC establishes fresh waters, observing a slight tendency to increase mineralization downstream, probably due to evaporation and leaching of salts by the circulating terrain.

The average nitrate levels (19.2 ± 3.9 mg/l) are relatively high, and the phosphate levels (0.21 ± 0.10 mg/l) are natural in rivers, providing an N/P ratio of over 16, a value that considers the balance for an aquatic ecosystem. Both anions are fundamental for soil activity, crop development, and good harvests.

Table b. Physicochemical parameters from sample waters of the Camiña River obtained in each locality.

	Chapiquilta	Camiña	Moquella	Francia
In situ				
Temperature (°C)*	17.54	17.30	21.97	19.19
DO (mg/l)*	5.01	4.83	4.65	6.68
ROP (mV)*	-1.8	-2.4	1.7	4.8
pH (U)*	7.51	7.57	7.97	7.72
EC (µS/cm)*	2,234	2,214	1,985	2,514
In laboratory (n=4)				
pH (U)	7.61 ± 0.10	7.78 ± 0.01	7.95 ± 0.01	7.89 ± 0.02
EC (µS/cm)	1,786 ± 57	1,754 ± 89	1,794 ± 134	2,280 ± 141
TDS (mg/l)	1,141 ± 18	1,155 ± 27	1,195 ± 18	1,479 ± 16
$N\text{-}NO_3^-$(mg/l)	16.4 ± 3.1	16.9 ± 0.8	24.6 ± 0.3	16.2 ± 0.2
$P\text{-}PO_4^{3-}$ (µg/l)	193 ± 12	324 ± 4	140 ± 5	107 ± 17
Percentual Na (%)	9.4 ± 0.7	9.7 ± 0.6	7.9 ± 0.6	10.2 ± 0.5
As (mg/l)	0.50 ± 0.04	0.51 ± 0.05	0.49 ± 0.04	0.47 ± 0.01
B (mg/l)	10.1 ± 0.40	9.00 ± 0.43	8.30 ± 0.40	10.2 ± 0.10

DO: dissolved oxygen; ROP: redox potential; EC: electrical conductivity; TDS: total dissolved solids.

The percentage of residual sodium obtained seems not to cause difficulties in crops developing, according to standards that allow a maximum level of 35%. The parameter measures the ratio between sodium concentrations and the sum of major cations in units of milliequivalents per gram per liter. For its part, the geochemical classification by dominant ions forms two types: sodium chloride in Chapiquilta and Camiña, and it changes to calcium-sodium chloride in Moquella and Francia. The ascending waters that emerge in springs, fountains, or thermal baths in the Central Andes are generally of the sodium chloride type, and once they circulate through fluvial terrains, they can incorporate calcium ions [5].

In figure 1, the Schoeller–Berkaloff diagrams are presented, maintaining the ionic relationships $Na^+ \sim Ca^{2+} > Mg^{2+} > K^+ // Cl^- \sim SO_4^{-2} >> HCO_3^-$. The average percentages were 55% for chloride and 41% for sulfate, and of the cations Na^+, Ca^{2+}, and Mg^{2+} were 45%, 41%, and 11%, respectively; these results suggest that waters had a low contribution of rainwater and a common origin, and the variations between locations may have different evolutionary pathways, mainly due to evaporation and leaching processes. The average concentrations of chloride and sulfate exceed the maximum permissible values for irrigation use (200 and 250 mg/l, respectively), limiting irrigation to less sensitive crops.

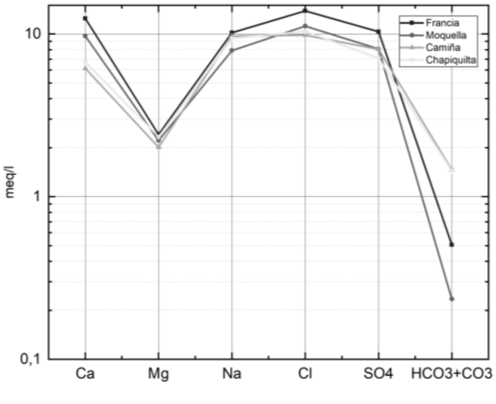

Figure 1. Schoeller Berkaloff diagram (major ions in meq/l units) for water samples from the four localities of the Quebrada de Camiña

The concentrations obtained for As (0.49 ± 0.02 mg/l) and B (10.3 ± 2.4 mg/l) exceed the water standards for irrigation use, which can generate adverse effects on crops and condition them to be tolerant to these metalloids [13, 28]. Weekly irrigation facilitates the accumulation in the soil and also the assimilation by the exposed biomass. The Food and Agriculture Organization (FAO) and World Health Organization recommend a maximum level of 0.10 mg/l for irrigation water and 0.01 mg/l for drinking water for As, just as Chile does in its NCh1333 and NCh409 standards, respectively [29, 30]. At low concentrations, B is essential for plant growth, but excesses in river waters can limit crops to only tolerable and semi-tolerable species such as vegetables; the Chilean standard allows a maximum permissible concentration of 0.75 mg/l and the FAO a reference value of 0.50 mg/l [29, 30]. Pincetti-Zuñiga et al. [6], determined the characterization of the waters in the Camarones River basin in the Arica and Parinacota region, show high concentrations of As, B, and salinity, which is mainly associated with the geological characteristics of the region, considering that the level of As increases in sodium chloride-type waters. The origin is also attributed to volcanism and leaching of ignimbrite rocks [5, 27]. The acid-base and redox properties predict the aqueous species $HAsO_4^{2-}$.

Physicochemical characteristics of soils and As fractionation

Environmental knowledge of soil chemistry has been fundamental in predicting the behavior of As on the surface of the lithosphere [4, 13], which can participate in dissolution, precipitation, methylation, sorption, and redox reactions, which in turn affect its distribution and mobility [16] and also in the choice of the sequential extraction procedure.

The basic statistics for the parameters, CF and I_{GEO}, for soils by locality are summarized in table c. In a spatial comparison by locality, it is observed that in general, they show few differences, but if compared transversally among themselves, there are differences between the soils of Chapiquilta and Camiña and those of Moquella and Francia. The average EC in the aqueous extract of the soils was 0.82 ± 0.19 dS/m, with lower values observed in Moquella and Francia. The salinity of the waters in the river course, the high evaporation rates, and the wind favor the transport, leaching, and precipitation of salts. Recent research by Figueroa and Newman [28] in the Arica and Parinacota region suggests using the proposal to classify soils as saline if the EC in a 1:5 aqueous extract is higher than 0.29 dS/m (for sandy soil), higher than 0.37 dS/m (for loamy soil), and if it is higher than 0.51 dS/m (for clay soil). It is often recognized that global distribution of saline soils is limited to arid and semi-arid zones.

The average pH value was 7.13 ± 0.50, considered neutral soils; however, in Chapiquilta and Camiña, they behave as slightly acidic, and in Moquella and Francia as slightly alkaline, which did not affect the mobility of As [10, 18]. In agreement with the pH measurements obtained, the percentages of $CaCO_3$ were quite low; even in Chapiquilta plots, it was not detected by the analytical method used and on average, did not exceed 6.2%. It is recognized that the optimal absorption of nutrients by most crops occurs with a pH close to neutrality. Regarding Easily Oxidable Organic Carbon (EOC) (2.5 ± 0.5%; on average), they present a slightly higher content in the Chapiquilta plots. The variability of organic matter and also pH can be attributed to the higher production of horticultural goods and cultivated area in this part of the territory, namely, in the order Camiña > Chapiquilta > Moquella and Francia, and to productive variables such as the use of guano and fertilizers, and the amount and frequency of irrigation. The characterization of the soils derived from this work in the upper part of the commune matches well with the data reported by Herrera et al. [22], in that area of the ravine.

Table c. Basic statistics of the physicochemical parameters and the contamination indices for As in the soils (based on dry weight).

	Localities (samples)			
	Chapiquilta (n = 4)	Camiña (n = 6)	Moquella (n = 6)	Francia (n = 4)
EC (µS/cm)	1,068 ± 37	916 ± 112	678 ± 99	590 ± 67
pH	6.82 ± 0.18	6.93 ± 0.26	7.44± 0.24	7.87 ± 0.34
$CaCO_3$ (%)	ND	6.3 ± 1.2	6.9 ± 0.1	5.8 ± 0.3
EOC (%)	2.9 ± 0.1	2.7 ± 0.4	2.6 ± 0.5	1.9 ± 0.4
$N\text{-}NO_3^-$(mg/kg)	259 ± 13	344 ± 31	151 ± 67	107 ± 11
$P\text{-}PO_4^{3-}$(µg/kg)	752 ± 80	496 ± 98	450 ± 261	484 ± 39
B (mg/kg)	40 ± 3	36 ± 7	18 ± 3	16 ± 1
As (mg/kg)	165 ± 24	122 ± 23	112 ± 20	99.8 ± 11.0
CF	8.3 ± 1.2	6.1 ± 1.1	5.6 ± 1.0	5.0 ± 0.5
I_{GEO}	0.74 ± 0.07	0.60 ± 0.09	0.57 ± 0.08	0.52 ± 0.05

EC: electrical conductivity; EOC: Easily oxidable organic carbon; CF: Contamination Factor; I_{GEO}: Geoaccumulation Index; ND: not detectable.

The nitrate content in the soils of Camiña and Chapiquilta was four times higher than in the lower part of the commune, recognized as a nutrient dependent on temperature, humidity, fertility, soil management, predecessor crop, and the state of the crop [31]; additionally, in the region, there are significant deposits of saltpeter in the Central Depression [23]. The concentrations of available phosphate were similar, except in one of the Moquella plots (PM1), which did not have any cultivated area. For nutrients of low solubility and mobility in soils, their availability for plant growth is regulated by geochemical and biological processes, with the assimilable form for plants being that which derives from organic matter. Nitrogen is always observed to dominate over phosphorus and is generally found in deficiency, replenished only through fertilization practices. The B levels in the soils match the interval of 23 ± 5 mg/kg reported in Camiña [22], although in the lower part of the ravine the concentrations are lower than those in Camiña and Chapiquilta (38.5 mg/kg). The baseline concentration of B considered in the soils of northern Chile is 10 mg/kg [32], and its origin is mainly due to chemical species rising through geothermal waters and dissolved borates being transported in a dynamic related to evaporation conditions [5].

The total As concentration obtained (124 ± 34 mg/kg), which is relatively high, is consistent with the average noted in cultivated soils of the Camiña Valley [22]. In this regard, it is known that As origin in northern Chile comes from volcanic episodes and the hydrochemical particularities of geothermal waters, and that arid conditions have limited its mobilization [5, 6, 7]. The maximum As concentrations permitted by International organizations in Canada and the USA are 12 and 22 mg/kg, respectively; in Australia, Bulgaria, the Czech Republic, Denmark, Poland, Sweden, and the United Kingdom, they reach a range between 15 to 20 mg/kg. Other countries such Finland, Norway, and Russia, have stricter regulations (not exceeding 5 mg/kg), meanwhile Belgium and Japan, which have more flexible measures [32, 33], similar to Peru, where a concentration of 50 mg/kg is allowed [34]. In Chile, there is a current legal regulatory gap. CF higher than 6 and I_{GEO} in soils are used to quantitatively assess contamination through total As concentrations in a particular matrix against a baseline reference in the territory, considered as 20 mg/kg for northern Chile [22]. These indices have been used by various authors in a comparative manner [12, 16], and the obtained values in our study demonstrate soil contaminated with As. No consistent correlations were obtained for As and other physicochemical parameters from soils, only a slight positive trend was associated with the increase in soil salinity ($R^2 = 0.79$).

Based on the presented background, it was interesting to determine associations of As with soil components using the harmonized sequential extraction procedure of the BCR. The results of As concentration and extraction percentages in the four stages of the procedure are shown in table d. According to them, the procedure was validated, as the sum of the concentrations of the four extracts was similar to the total concentration of As determined by total acid digestion. The mobility in the first three consecutive stages was low (≤ 21%), with the soils exhibiting very similar behavior, as As was mostly associated with the residual fraction (≥ 79%). These results confirm that As is found in the soils as insoluble and non-bioavailable compounds, that exhibit low mobility in response to pH decrease and redox conditions; insoluble compounds can be sulfide minerals and lithogenic in origin .

Table d: As concentration in mg/kg and % at the steps of the BCR protocol from soils samples of Chapiquilta, Camiña, Moquella, and Francia plots.

	PCh1		**PC2**		**PM3**		**PF2**	
Step	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
1	14	7	6	4	4	4	7	8
2	14	7	11	8	8	8	6	7
3	11	6	8	6	6	6	5	6
4	152	80	115	82	88	83	68	79

Arsenic concentration in vegetables

For Camiña garlic plants per plot, the results obtained for As in the root, stem, bulb, and leaf samples, and BAF and TF are shown in table e. Garlic plants seems to behave as As phytoremediator just like white corn plants [22], as both vegetables have the ability for bioaccumulation As in the root part and can be used in intercropping as a method to remediate As in soils, as proposed by Wang et al. [35]. The average As concentration in the root samples was 177 ± 18 mg/kg, and it appears to be absorbed in similar concentrations (30% of the samples) and higher (70% of the samples) than those present in the soil, which is reflected in the determined BAFs close to 1 and 2. The accumulation of the metalloid in the root was slightly higher in plants grown in soils with lower levels of As, although no correlation was found between the matrices. Vegetable accumulation depends on the availability of metalloids, which some plants can increase by releasing either organic or inorganic materials in root exudates; in rice plants, for example, 60% of the total As was found in the roots [11]. Arsenate anions in the soil solution can be absorbed by plant roots in a process that may be similar to that of other essential nutrients like phosphate and then transported through the vascular system by passive diffusion or through active transport mechanisms that the plant uses to move nutrients and other ions [12 - 14]. Arsenite and As methylated species can also be assimilated [9], we hypothesized that due to low levels of phosphate and high nitrate contents in soils, the waters used for crops irrigation have an impact on the absorption of available As species, however this possibility was not addressed in this research.

Table e. Total As concentration, BAF and TF in garlic plant tissue from Francia and Camiña (mg/kg on dry weight).

Tissue		Francia		Camiña		
		PF1	PF2	PC1	PC2	PC2
Root	As	166 ± 3	179 ± 10	200 ± 7	177 ± 30	162 ±7
	BAF	1.74 ± 0.02	1.74 ± 0.02	2.13 ± 0.12	1.30 ± 0.35	1.21 ±0.03
Stem	As	90.0 ± 4.2	84.5 ± 5.0	72.3 ±1.0	84.5 ± 4.9	72.3 ±1.0
	BAF	0.943 ± 0.006	0.820 ± 0.011	0.751 ± 0.015	0.614 ± 0.027	0.564 ± 0.016
	TF	0.542 ± 0.035	0.472 ± 0.001	0.352 ± 0.012	0.487 ± 0.110	0.465 ± 0.026
Bulb	As	0.357 ± 0.006	0.470 ± 0,011	0.481 ± 0,004	0.443 ± 0.004	0.507 ± 0.004
	BAF/ 10^{-4}	37 ± 1	46 ± 6	51 ± 5	32 ± 3	38 ±1
	TF1/ 10^{-3}	4 ± 1	6 ± 1	7 ± 2	5 ± 1	7 ±1
Leaf	As	0.072 ± 0.016	0.056 ± 0.011	0.118 ± 0.006	0.061 ± 0.007	0.059 ± 0.009
	BAF/ 10^{-4}	8 ± 1	5 ± 1	13 ± 2	4 ± 1	4 ±1
	TF2	0.201 ± 0.028	0.119 ± 0.021	0.244 ± 0.011	0.138 ± 0.014	0.115 ± 0.008

BAF: bioconcentration factor; TF: stem-root translocation factor; TF1 bulb-stem translocation factor; TF2 leaf-bulb translocation factor

The development of crops with both waters and soils naturally contaminated with As produces accumulation in the root and stem, 68% and 38% of the total in garlic plants, respectively. The biomass of the stem samples, exposed in the rhizosphere, showed an average of 81.0 ± 8.1 mg/kg, but the determined TFs were variable and less than 1, which follows the order of bioaccumulation in the plant. The root mobilizes As species to the stem, obtaining average translocation factors of 0.46 ± 0.68. The leaves and roots originate from the stem; and the stem is situated at the base of each clove within the bulb.

The peeled garlic cloves, that make up the bulb, contained an average As concentration of 0.451 ± 0.054 mg/kg, and the very low accumulation percentages indicate that it does not pose a consumption risk, considering the current regulations in Chile corresponding to Reglamento Sanitario de los Alimentos establishes a maximum As concentration in food of 1.0 mg/kg [36]. These results are relevant for the population of Tarapacá who purchase Camiña white garlic at public markets, agricultural terminals, and on-site sales. The lower bioaccumulation of As in the bulb was reflected in BAF values and also in TF1 between stem and bulb, which were slightly greater than 0.004 units. For their part, it was observed that the leaf tissues did not show an appreciable concentration of the metalloid, averaging 0.073 ± 0.025 mg/kg, but was determined to exhibit a relatively higher translocation from the bulb to the leaves, with TF2 values ranging between 0.12 and 0.24 units. The accumulation of As in the roots and stem instead of the bulb and leaves may be due to several factors related to the plant's physiology or the characteristics of the plant parts, which predicts protection for photosynthesis in the leaves and detoxification in the bulb. We did not find available information on the normal As content in garlic cloves.

Finally, the results obtained from the statistics of total As concentration in freeze-dried beetroot and carrot samples and BAF are shown in table f. Both root vegetables absorbed relatively low As concentrations in the edible part of the plants that are developed at the rhizosphere, with an As average of 4.45 ± 0.98 mg/kg in beetroots and very fluctuating values of 3.26 ± 3.50 mg/kg in carrots, that exceed several folds the maximum concentrations allowed for As in food in several countries such Chile (1 mg/kg), UK (1 mg/kg) and China (0.5 mg/kg) [20, 36]. In soils contaminated with 60 mg/kg of As from the locality of Chiu Chiu (Antofagasta region, northern Chile), lower concentrations of As were reported in beetroot (0.62 ± 0.05 mg/kg) and carrot (0.52 ± 0.04 mg/kg), and much lower As levels in the same vegetables cultivated in Spain [9], compared to our results. In contrast, the fieldwork by Bergqvist et al. [11] in soils contaminated with 142 mg/kg of As demonstrated that carrots assimilated As at an average of 4.04 ± 1.21 mg/kg. The study of Caporale et al. [4]. It was determined that carrot crops grown in volcanic soils with 20 mg/kg of arsenic and irrigated with water containing 3-6 mg/l of arsenic showed arsenic levels between 1.79 and 5.43 mg/kg in the vegetables. These levels are similar to those found in the edible biomass cultivated in Chapiquilta, which resulted in an impact on plant growth and photosynthetic rate. Values below 0.045 for BAF in beetroot and carrot reflect low bioaccumulation from the soil and irrigation water.

According to the set of results obtained, it is deduced that As can be retained in the soil and also mobilized or absorbed in vegetable crops, mainly in the root and stem of garlic plants, due to the continuous supply of As anions in the waters of the Camiña River, used for irrigation, which can leach As from the soil. Figure 2 shows the total concentrations of As in a graph the boxplot, obtained in the matrices under study in the order of garlic root > soil > garlic stem >> beetroot > carrot > water > garlic > garlic leaves.

Table f. Concentration of total As and BAF in beetroot and carrot samples crops from Chapiquilta and Moquella (mg/kg on dry weight).

Locality	Plot	Sample	As	BAF
Chapiquilta	PCh1	Carrot	3.76 ± 2.83	0.023 ± 0.017
	PCh2		6.38 ± 3.02	0.041 ± 0.018
Moquella	PM2		0.895 ± 0.078	0.008 ± 0.001
	PM3	Beet	5.66 ± 0.09	0.045 ± 0.001
			3.60 ± 0.40	0.028 ± 0.003
			4.09 ± 0.10	0.032 ± 0.001

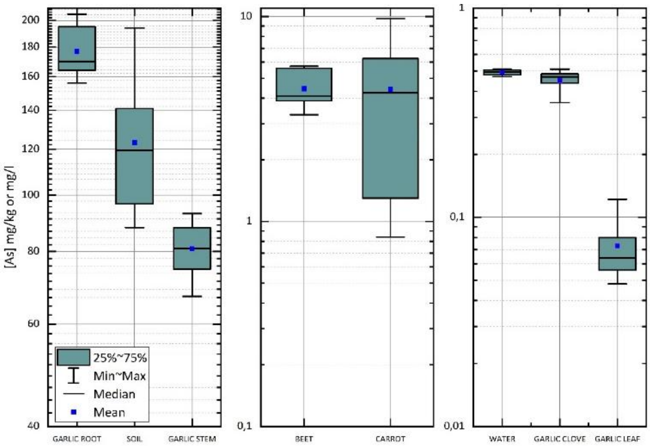

Figure 2. Boxplot diagram of As concentration (mg/kg or mg/l) was obtained in the sample matrices (a) garlic plant roots, cultivated soil, and garlic plant stem; (b) beetroot and carrot; and (c) irrigation water, and bulbs and leaves of the garlic plant.

CONCLUSION

The waters of the Camiña River are fresh, slightly alkaline, contaminated with B, of the sodium chloride and sodium calcium chloride type, and mobilize As ($HAsO_4^{2-}$) levels that quintuple the standards. The water used for irrigation increases As content in arable soils and in harvest vegetables.

The cultivated soils in the region are saline, neutral, with low calcium carbonate and organic matter content but with high levels of B and naturally contaminated with As, show differences between the upper and lower parts of the ravine; the highest concentrations of As, B, nitrate, and salinity are observed in Chapiquilta and Camiña. The obtained CF-I_{GEO} indicates As contamination, and the operational speciation of the BCR is conclusive in showing slight mobility from the soil and is mostly associated with the residual fraction, confirming the lithogenic origin of the metalloid.

White garlic plants act as phytoremediators of As, bioaccumulating in the root. Translocation from the root to the plant stem is observed, with lower bioaccumulation in this tissue. The bulb, the edible part of the vegetable, and the leaves do not pose a risk for food consumption, and the limited translocation predicts protection for photosynthesis in the leaves and detoxification in the bulb.

The concentrations of As in soils are assimilated in the development of beetroot and carrot crops, exceeding the regulated and suggested concentrations in food by three to six times. The observed fluctuations values in carrot As concentration are difficult to interpret.

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REFERENCES

1. B. Mandal, K Suzuki, *Talanta.* **58**, 201-235, (2002)
2. D. López, J. Bundschuh, P. Birkle, M. Armienta, L. Cumbal, O. Sracek, L. Cornejo, M. Ormachea, *Sci. Total Environ.* **429**, 57-75, (2012)
3. L. Cornejo, H. Lienqueo, P. Vilca, Desalin. *Water Treat.* **153**, 36-45, (2019)
4. A. Caporale, P. Andamo, S. Azam, M. Rao, M. Pigna, *Chemosphere.* **193**, 464-471, (2018)
5. J. Tapia, B. Schneider, M. Inostroza, F. Álvarez, J. Luque, F. Aguilera, S. Parra, M. Bravo, *J. S. Am. Earth Sci.* **105**: 102905, (2021)
6. G. Pincetti-Zuñiga, L. Richards, L. Daniele, A. Boyce, *Sci. Total Environ.* **806**, 150206, (2022)
7. A. Issanov, B. Adewusi, N. Saint-Jacques, T. Dummer, *Toxicol. Appl. Pharmacol.* **483**, 116808, (2024)
8. L. Romero, H. Alonso, P. Campano, R. Fanfani, R. Cidu, C. Dadea, T Keegan, M. Farago, *J. Appl. Geochem.* **18 (9)**, 1399-1416, (2003)
9. I. Pizarro, M. Gómez-Gómez, J. León, D. Román, M. Palacios, *Sci. Total Environ.* **565**, 557-563, (2016)
10. A. Vandeurem, B. Pereira, A. Kaba, H. Titeux, P. Delmelle, *Sci. Total Environ.* **902**, 166073, (2023)
11. C. Bergqvist, R. Herbert, I. Persson, M. Gregor, *Environ. Pollut.* **184**, 540-546, (2014)
12. V. Antoniadisa, E. Levizou, S. M. Shaheen, Y. Sik Ok, A. Sebastian, C. Baum, M. Prasad, W. Wenzel, J. Rinklebe, *Earth-Sci. Rev.* **171**, 621-645, (2017)
13. I. Khan, S. Afzal Awan, M. Rizwan, S. Ali, X. Zhang, L. Huang, *Environ. Pollut.* **286**, 117389, (2021)
14. S. Singh, J. Karwadiya, S. Srivastava, P. Kumar Patra, V.P. Venugopalan, *Ecol. Eng.* **175**, 106476, (2022)
15. Z. Chi, K. Pi, Y. Wu, X. Xie, Y. Wang, *Ecotoxicol. Environ. Saf.* **283**, 11625, (2024)
16. T. Zhang, B. Zheng, M. Wang, J. He, S. Xia, *Gondwana Res.* **130**, 131-139, (2024)
17. Ph. Quevauviller. *Trends Anal. Chem.* **17(10)**, 632-642, (1998)
18. T. Karak, O. Albollino, P. Bhattacharyya, K. Das, R. Paul, *Chemosphere* **85**, 948-960, (2011)
19. K. M. Upadhyay, A. Shukla, P. Yadav, S. Srivastava, *Food Chem.* **276**, 608-618, (2019)
20. M. Varol, K. Gündüz, M. Ras¸ I. Sünbül, H Aytop, *Environ. Res.* **206**, 112252, (2022)
21. R. Calderón, J. García-Hernández, P. Palma, J. B. Leyva-Morales, M. Godoy, M. Zambrano-Soria, P. J. Bastidas-Bastidas, G. Valenzuela, *J. Food Compos. Anal.* **123**, 105527, (2023)
22. V. Herrera, C. Carrasco, P. Sandoval, C. Cortés, *Rev. Soc. Quim. Perú.* **83(1)**, 52-64, (2017)
23. E. Lictevout, C. Maass, D. Córdoba, V. Herrera, R. Payano, "Recursos Hídricos, Región de Tarapacá: Diagnóstico y Sistematización de la Información" Centro de Investigación y Desarrollo de Recursos Hídricos-CIDERH - Universidad Arturo Prat, Iquique, 223p. 2013
24. APHA-AWWA-WPCF. "Métodos normalizados para el análisis de aguas potables y residuales" Ediciones Díaz de Santos, S.A.; Madrid, España. 1830p. 1992
25. E. Custodio, M.R. Llamas, "Hidrología Subterránea". Ediciones Omega SA, Barcelona, 2350p. 1983
26. A. Sadzawka, M.A. Carrasco, R. Grez, M.de la L. Mora, H. Flores, A. Newman. Serie Actas. Instituto de Investigaciones Agropecuarias, CRI La Platina, Santiago, Chile. 2006
27. N. Morales-Simfors, J. Bundschuh, I. Heralh, C Inguaggiato, A. Caselli, J. Tapia, F. Apaza, M. Armienta, M. Ormachea, E. Joseph, D. López. *Sci. Total Environ.* **716**, 1-32, (2020)
28. L. Figueroa, A. Newman, *Idesia.* **41**, 133-137, (2023)
29. FAO, "Water Quality for Agriculture Irrigation and Drainage Paper 29 Rev 1". Ayers R.S.; Westcot D.W. 1985
30. Norma Chilena NCh 1333. Requisitos de calidad del agua para diferentes usos. Diario Oficial de la República de Chile, Santiago, Chile, 22 de mayo de 1987. Norma Chilena NCh 409/1."Agua potable-1-Requisitos". Diario Oficial de la República de Chile, Santiago, Chile, 27 de junio de 2006.
31. Mazzilli S, Ernst O, Sastre A, Terra G. *Agrociencia Uruguay* **19,** no.1 (2015).
32. S. Cortes, E. Reynaga-Delgado, A.M. Sancha, C. Ferreccio, *Sci. Total Environ.* **410-411**, 96-101, (2011)
33. S. Chen, M. Wang, *Journal of Integrative Agriculture*, **17 (4)**, 765-774, (2018)
34. Norma Peruana Decreto Supremo N° 011-2017-MINAM de Estándares de Calidad Ambiental (ECA). Perú, 2017
35. W. Wang, X. Yang, Q. Mo, Y. Li, D. Meng, H. Li. *Ecotoxicol. Environ. Saf.* **259**, 115004, (2023)
36. Ministerio de Salud, División Jurídica. Reglamento Sanitario de los Alimentos; Decreto Supremo DS977, Santiago, Chile, 1996