

Availability and Distribution of Arsenic in a Corn Crop in the Eastern Zone of the Province of Tucumán, Argentina

María del Pilar Balverdi^{1*} , Emilce Viruel² , Marcela Ferrero³ ,
Adriana María Sales¹ 

How to cite:

Balverdi et al. 2023. “Availability and Distribution of Arsenic in a Corn Crop in the Eastern Zone of the Province of Tucumán, Argentina”. *Journal of Agricultural and Food Chemical Engineering* 3(4): 1 – 13. <https://doi.org/10.58612/jafce341>

Received:

May 23, 2023

Accepted:

June 9, 2023

Published:

June 17, 2023

Corresponding author:

María del Pilar Balverdi
pilarbalverdi@gmail.com

¹Institute of Analytical Chemistry. Faculty of Biochemistry, Chemistry, and Pharmacy. National University of Tucumán. Ayacucho 471, T4000INI. Tucumán. Argentina.

²Animal Research Institute of the Semiarid Chaco (IIACS). Agricultural Research Center (CIAP). National Institute of Agricultural Technology (INTA). Chañar Pozo s/n (4113). Tucumán. Argentina.

³YPF Tecnología (Y-TEC) Av. del Petróleo Argentino 900-1198, Berisso, Buenos Aires, Argentina.

Abstract: There is a relationship between the arsenic content of crops and that of agricultural soils and the water used for irrigation. The consumption of foods with high arsenical concentrations represents a health risk. Corn is one of the most widely grown cereals in the world due to its ability to adapt to different soils and climates. In northern Argentina, the cultivation of this plant has become more important over the years. However, the groundwater supply of this zone has high arsenic levels. In this study, the levels and distribution of arsenic and its species in soils and corn plants of this agricultural area were determined. Some of the edaphic characteristics that facilitate its phytoavailability were also studied, and the rate of transfer and accumulation of the metalloid in the plant was determined. Elemental determinations were carried out by ICP-MS, FAAS and UV-VisS. Arsenical species were analyzed by HPLC-ICP-MS. We found that the soil is not contaminated with arsenic and that the proportion of the metalloid passing into the aqueous phase is low. However, a high proportion of this available arsenic is taken up by the plant. Although it was not detected in the cob kernels, the concentrations of arsenic in the roots and leaves of the plants are high, which represents a risk for its use as fodder. As(V) was dominant in the system. Methylated species were quantified in the plants even though they were not detected in the soil.

Keywords: phytoavailability, agricultural soil, bioaccumulation, arsenical species

1. Introduction

Plants can absorb and store nutrients and contaminants from the growing soil. Then, these elements are transferred to the other levels of the food chain through feeding. When the concentration of potentially hazardous elements transferred is high, it can represent a risk to human and animal health (Meharg and Hartley-Whitaker, 2002; Yañez *et al.*, 2019). There are studies that establish a significant correlation between the arsenical content of crops with that of agricultural soils and the water used for irrigation (Su *et al.*, 2009; Sadee *et al.*, 2016; Ruiz Huerta *et al.*, 2017). Because of this, national and international control agencies established a maximum value of 20

mg kg⁻¹ for total arsenic in crop soils (EPA, 2012). However, it is necessary to evaluate how much of this arsenic and its species are available for the plant uptake (Norton *et al.*, 2012), since variations in the physicochemical characteristics of the soil and rhizospheric soil (portion of the soil closely linked to the plant root), can alter the content of arsenic species, modifying the solubility of arsenic minerals and subsequent uptake of the element by the plant (Jedinak *et al.*, 2009; Punshon *et al.*, 2017). Then, in order to be absorbed by the plant, arsenic must be mobilized from the mineral structures to the aqueous phase of the soil (Ursitti *et al.*, 2004). Different extraction methods have been used to determine the mobility of soil elemental components. The natural mobility of elements can be estimated by evaluating their solubility in water, in this way the most soluble phases of the soil are washed out without altering the mineralogy. The concentrations of elements extracted are low, but may represent the most easily mobilizable fraction of the soil (Anawar *et al.*, 2008; Baig *et al.*, 2010; Martínez Sánchez *et al.*, 2011).

Arsenic toxicity varies according to the species: As(III) is more toxic than As(V), and inorganic species are more toxic than organic species (IARC, 2012). The arsenic species mostly found in food crops are As(III), As(V), MMA (monomethylarsonic acid) and DMA (dimethylarsinic acid) (Ruttens *et al.*, 2018). The consumption of foods with high concentrations of arsenic can mean a significant risk of poisoning. The transfer of arsenic absorbed in the food crops to humans can occur directly, or indirectly through animals that consume the plant (Kachenko *et al.*, 2010; Zhao *et al.*, 2010). To quantify the capacity of plants to accumulate trace elements, the Bioaccumulation Index (BAI) was settled, which establishes the relationship between the amount of contaminant in a living organism and the amount of that contaminant in the environment (Kabata-Pendias, 2004). Quantitative extraction of elemental species, without altering their proportion, is important in speciation studies. Several extraction methods have been developed for arsenic speciation in plants, using extractants such as methanol, water and different mixtures of surfactants (Sadee *et al.*, 2016). Sodium dodecyl sulfate (SDS) is a surfactant capable of breaking down water-insoluble protein complexes and has a high extraction efficiency for arsenical species. (Jedinak *et al.*, 2009). Corn (*Zea mays* L.) is one of the most widely cultivated cereals in the world. It is used as food and for the preparation of starch, oil, alcoholic beverages, fodder and ethanol (Tiwari and Yadav, 2019). The province of Tucumán, located in the northwest of Argentina, has optimal soil characteristics for the cultivation of cereals, which is why the cultivation of corn has gained special relevance in the last decade, becoming an important part of the economy of the region. The eastern part of the province belongs to the Chaco-Pampean Plain, which is the largest geographic region in South America with high arsenic concentrations in its groundwater supplies (Nicolli *et al.*, 2012). Previous studies carried out in the province reported that the arsenic content in its surface and groundwater is higher than the limit of 10 µg L⁻¹ established by the WHO (García *et al.*, 2000; Maizel *et al.*, 2018). Nicolli *et al.* (2012) have reported that elevated arsenic concentrations are due to the volcanic components of the loessic deposits that characterize the area. This may represent an important health problem for the exposed population, as local crops are susceptible to contamination.

The objective of this work was to determine the mass fraction (mg/kg) of arsenic and its species present in soil and corn plants of a crop in eastern Tucumán province, Argentina. The fraction of these elements that is transferred, accumulated and distributed in the plant was determined to evaluate the potential hazard the consuming population is exposed to.

2. Materials and Methods:

2.1. Sampling

The department of Leales is located in the southeast of the province of Tucumán, Argentina. Soil and corn plant samples were taken from a field located at 27°11'34" South latitude and 65°14'47" West longitude, at an altitude of 435 m a.s.l. This area belongs to the depressed saline plain of Tucumán, characterized by the presence of a water table with a high saline content and few natural drainage networks. It has a semi-arid subtropical climate with a dry season, and rainfall (mostly in the wet season) between 500 and 650 mm per year, an average annual temperature of 19.5°C, with a variation in July of 12.8 °C and 27.1 °C in January. The soil in the area is the Haplustol Fluventic type with silt loam texture, Table 1 shows their physicochemical characteristics at the beginning of the study.

Table 1. Physicochemical properties of the soil ($\bar{x} \pm SD$).

Sand (%)	15.2 ± 0.2
Silt (%)	70.3 ± 0.8
Clay (%)	14.5 ± 0.1
Moisture (%)	21.6 ± 0.5
Density (g/cm ³)	2.38 ± 0.17
Apparent density (g/cm ³)	1.14 ± 0.28
Porosity (%)	55.1 ± 0.5
pH (0 – 20 cm)	7.2 ± 0.2
pH (20 - 30 cm)	8.0 ± 0.1
EC (dS.cm ⁻¹)	2.2 ± 0.6
Organic matter (%)	2.50 ± 0.05

We worked with the whole corn plant, the soil and the rhizospheric soil. At each sampling site, corn roots, stems, leaves and kernels were sampled. In addition, approximately 2.0 kg of soil were taken from a depth of 0 to 25 cm directly under the harvested plant and close to the roots, using a clean shovel. The plant parts were washed with ultrapure water (18 MΩ cm) and dried in an oven. The soil and the rhizospheric soil (which was separated from the roots) samples were oven-dried at 42 °C for 2 hours, allowed to cool, and passed through a 2 mm sieve.

2.2. Samples treatments

Acid digestion

An acid digestion process was carried out on all samples (plant roots, stems, leaves, grains, soils and rhizospheric soils). Approximately 100.0 mg (± 0.2 mg) of each sample was accurately weighed using a Mettler Toledo AG245 analytical balance. Then, 1 mL of concentrated and redistilled HNO₃ (Merck, Darmstadt, Germany) and 1 mL of hydrogen peroxide 30 vol (Cicarelli, Santa Fe, Argentina) were added. 0.1 mL of hydrofluoric acid 48 % (Merck, Darmstadt, Germany) was added to the soil and rhizospheric soil samples. All samples were heated for 24 hours. They were then centrifuged at 7000 rpm for 5 min using a refrigerated ultracentrifuge U-320R (Boeco, Hamburg, Germany). All reagents used were of analytical grade.

Extraction processes

Two extraction processes were performed on the samples: on the one hand, water was used as an extraction agent to analyze the elements that were naturally mobilized to the aqueous phase of soil and rhizospheric soil samples, on the other hand, SDS-Tris-HCl was used to extract arsenical species from the plant tissue of corn plants.

Soil and rhizospheric soil samples were taken as follows: about 1000 mg (± 0.2 mg) of the sample were accurately weighed on an analytical balance and 250 mL of ultrapure water (18 M Ω cm) were added. They were left in contact for 24 h and then centrifuged at 3000 rpm for 5 min. The supernatants were stored in polypropylene tubes for further analysis.

The extraction of arsenical species in the corn plant was carried out as follows: 500.0 mg (± 0.2 mg) of each plant part (root, stem, leaf and grain) was weighed on an analytical balance and 4 mL of SDS-Tris-HCl solution was added. They were placed in an ultrasonic cleaner (Testlab, Buenos Aires, Argentina) for one hour and centrifuged at 7000 rpm for 10 minutes. To avoid alterations in the extracted arsenic species, the supernatants were stored in opaque polypropylene tubes and kept at 4 °C until use.

2.3. Elemental determinations

Concentrations of iron, manganese, total arsenic, calcium, magnesium and phosphorus were determined in the digests of all samples and in the aqueous fractions of soil and rhizospheric soil.

Iron, manganese and total arsenic were determined by ICP-MS (PerkinElmer SCIEX - ELAN DRCII-e, Thornhill, Canada). High purity Argon gas (99.996%) was used as plasma (13.5 L min⁻¹), auxiliary gas (1.2 L min⁻¹) and nebulization (0.85 L min⁻¹). A multi-element standard for ICP (Merck CertiPUR, Darmstadt, Germany) was used to carry out the measurements.

Standards of 40, 80, 100, 120, and 150 $\mu\text{g L}^{-1}$ of As, Fe, and Mn were prepared. The 3.4 version of the ELAN ICP-MS Instrument Control Software program was used. This program allowed us to eliminate the percentage of intensity from the signal of interest due to the isobaric interferences present, for which the isotopes ⁷⁵As, ⁵⁷Fe, ⁵⁵Mn were selected.

The presence of calcium and magnesium was determined by a Perkin-Elmer AAnalyst 100 atomic absorption spectrometer (Norwalk, USA). Air-acetylene flame (APHA,

AWWA, WPCF, 1992) and hollow cathode lamps were used, with a wavelength of 422.7 nm for Ca and 285.2 nm for Mg. Standards of 0.4, 1.0, 2.0, 4.0, 5.0 mg L⁻¹ Ca, and 0.1, 0.2, 0.3, 0.4, 0.5 mg L⁻¹ Mg were prepared from commercial standards of 1000 mg L⁻¹ of each element (Merck certiPUR, Darmstadt, Germany). SrCl₂ 10% was used as a releasing agent and KCl 10% as an ionization suppressant.

The presence of phosphorus was determined by the modified vanadomolybdophoric acid method (APHA, AWWA, WPCF, 1992). A Biotraza 722 spectrophotometer (GEA S.R.L., Santa Fe, Argentina) was used. Standards of 3.0, 4.0, 5.0, 10.0, 15.0 and 20.0 mg L⁻¹ of P were prepared from anhydrous KH₂PO₄ (Cicarelli, Santa Fe, Argentina) and an aqueous solution of molybdate-vanadate from (NH₄)₆Mo₇O₂₄·4H₂O (Cicarelli, Santa Fe, Argentina) and NH₄VO₃ (Merck, Darmstadt, Germany) were used.

2.4. Determination of arsenic species

To quantify the arsenical species in the system, SDS-Tris-HCl extractions performed on the corn plant, and the aqueous fractions of the soil and rhizospheric soil were analyzed. An HPLC (PerkinElmer LC-pump series 200 systems, Norwalk, USA), with an ion exchange column (Hamilton PRP X-100, 250 mm x 4.6 mm) and a 100 µl loading loop was used. Ammonium dihydrogen phosphate 20 mM (Merck Millipore, Darmstadt, Germany) was used as the mobile phase at pH 5.6 with a flow rate of 1 mL min⁻¹. Standards of arsenical species of 10 µg L⁻¹, prepared from solid drugs, were used. The standards used were As(III) of diarsenic trioxide (As₂O₃, Sigma, St. Louis, USA), As(V) of diarsenic pentoxide (As₂O₅·2H₂O, Aldrich, St. Louis, USA), DMA and MMA prepared from sodium methyl arsenate (CH₃AsO(ONa)₂·6H₂O, Merck, Darmstadt, Germany). All prepared solutions were stored at 4 °C until their use. The area of each resulting peak of the chromatograms was analyzed using the Origin 8.0 software.

2.5. Figures of merit

Linearity, limits of detection (LOD), limits of quantification (LOQ) and recovery studies were performed. The LOD and LOQ values for each element were determined by 10 replicates of the sample preparation blank and calculated as three times and ten times the standard deviation divided by the slope. The calibration curves showed good correlation coefficients. The measurement of each sample was performed in triplicate. Recovery values between 89 and 135% were obtained in all cases.

3. Results and Discussion

3.1. Total arsenic, arsenic species, and other elements analyzed in the soil and rhizospheric soil

Table 2 presents the content of total arsenic, phytoavailable arsenic, and arsenic species present in the soil and rhizospheric soil samples. The contents are expressed in mass fraction (mg kg⁻¹), based on the dry weight of the sample.

Table 2. Mass fractions (mg kg⁻¹) of arsenic in soil and rhizospheric soil ($\bar{x} \pm SD$).

Sample	¹ As _T (mg kg ⁻¹)	² As _D (mg kg ⁻¹)	³ % _{ext}	⁴ As(III) (mg kg ⁻¹)	⁴ As(V) (mg kg ⁻¹)	⁴ MMA (mg kg ⁻¹)	⁴ DMA (mg kg ⁻¹)
Soil	7.7±0.1	0.130±0.002	1.7%	0.00060±0.00005	0.082±0.002	ND	ND
Rhizosphere	8.38±0.09	0.126±0.005	1.5%	ND	0.058±0.002	ND	ND

¹As_T: Total arsenic mass fraction in soil and rhizospheric soil.

²As_D: Phytoavailable arsenic mass fraction, quantified in the aqueous phase of the soil and the rhizospheric soil, using ultrapure water as extraction agent.

³%_{ext}: Fraction of arsenic that is mobilized from the soil and the rhizospheric soil into the soil solution.

⁴As(III), As(V), MMA, DMA: Arsenic species extracted from the soil and the rhizospheric soil using water as extraction agent.

ND: Not detected

The mass fraction of total arsenic in the soil and rhizospheric soil was around 8 mg kg⁻¹, while its mass fraction in the aqueous phase was much lower (0.130 mg kg⁻¹). These levels were below the 20 mg kg⁻¹ limit established by control agencies (EPA, 2012). This indicated that it is an agricultural soil with low arsenic levels. Similar values have been reported for crop soils in Europe and Africa, with concentration ranges from 0.2 to 20 mg kg⁻¹ (Marwa *et al.*, 2012; Tóth *et al.*, 2016).

The extraction fraction (%_{ext}) corresponded to the quotient between the arsenic in the aqueous extraction solution and the total arsenic in soils and rhizospheric soil. The percentage of arsenic mobilized from the solid phase to the aqueous phase was of 1.6% on average. The value obtained is relatively low since arsenic mobilization ranges are from 0.45 to 18.88% (Rosas Castor *et al.*, 2014). A low mobilization rate indicates that the soil effectively retains the arsenic present in the solid phase. The physical and chemical factors that may be responsible for the low availability of arsenic in the studied system were analyzed. As indicated in Table 1, we worked with soil with a silty loam texture, with pH values of 7.2 in its upper horizon, and 8.0 in deeper layers. Under these conditions, arsenic behavior is highly reliant on oxygenation, which itself depends on soil density, porosity and texture (Neira *et al.*, 2015). Under conditions of low oxygenation the inorganic species As(III) predominates, which is not retained by the charged soil particles and consequently mobilizes vertically towards deep layers away from the upper horizon. When oxygenation is higher, the predominant form is the inorganic species As(V), which is adsorbed on the different soil particles (organic matter, clays, minerals) and consequently is not very mobile and is not easily removed from the upper horizon (Sadiq, 1997). Although the toxicity of As(V) is lower than that of As(III), its immobilization makes it potentially more dangerous for biotransfer and any change in the physicochemical conditions of the soil can increase the phytoavailability of the element (Wang and Mulligan, 2006). The studied system had good values of density (2.38 g.cm⁻³) and porosity (55.1%), indicating that it was a soil with good oxygenation (Neira *et al.*, 2015). Under these conditions, it could be considered that As(V) would be the dominant species in the soil. This was confirmed by analyzing the quantification data in Table 2. In the soil, inorganic species As(III) and As(V) were observed, while in the rhizospheric soil only the inorganic species As(V) was detected. The mass fractions obtained for As(V) are higher than those of As(III).

Organic arsenic species were not detected in any of the soil and rhizospheric soil samples.

Table 3 shows the mass fractions of calcium, magnesium, iron, manganese and phosphorus present in the soil and rhizospheric soil samples. These elements are of interest for the analysis of arsenic mobility.

Table 3. Mass fractions (mg kg⁻¹) of calcium, magnesium, iron, manganese and phosphorus in soils and rhizosphere samples ($\bar{x} \pm SD$).

Elements	¹ S _T	² R _T				
Ca	366.4 ± 3.4	450.6 ± 14.6				
Mg	5364.0 ± 34.1	9218.4 ± 250.1				
Fe	4804.1 ± 79.6	4812.1 ± 162.4				
Mn	510.0 ± 4.4	528.4 ± 4.2				
	¹ S _T	² R _T	³ S _D	⁴ R _D	⁵ S% _{ext}	⁶ R% _{ext}
P	1062.4 ± 22.0	1658.2 ± 23.2	2.80 ± 0.05	9.00 ± 0.05	0.26	0.54

¹S_T: Total mass fraction of the element in the soil samples.

²R_T: Total mass fraction of the element in the rhizosphere samples.

³S_D: Total mass fraction of the element in the soil aqueous phase.

⁴R_D: Total mass fraction of the element in the rhizosphere aqueous phase.

⁵S%_{ext}: Percentage of P mobilized from the soil to the soil aqueous phase.

⁶R%_{ext}: Percentage of P mobilized from the rhizosphere to the aqueous phase of the rhizosphere.

In the soil, the magnesium mass fraction is around 5000 mg kg⁻¹, while the calcium mass fraction is around 350 mg kg⁻¹. For both elements, a rhizospheric effect is observed, which produces an increase in the rhizospheric soil mass fractions of 72% for magnesium and 23% for calcium, data reported in the literature for corn crops (Rosas Castor *et al.*, 2014). It has been disclosed that, under the pH and oxygenation conditions present in this crop, Ca and Mg form oxides and hydroxides which have a high affinity for As(V), promotes immobilization (Galindo *et al.*, 2000). Lin *et al.* (2004) also indicate that Ca favors the adsorption of arsenic on the surface of organic matter. The concentration of these elements and the high proportion of soil organic matter (2.5%), are factors that could explain the low mobilization of arsenic in the system.

Total iron and manganese in the studied agricultural system were around 4800 mg kg⁻¹ and 500 mg kg⁻¹, respectively. It has been reported that iron and manganese from minerals present in the soil, and rhizospheric soil form amorphous oxides and hydroxides, could adsorb arsenic species on their surface, immobilizing them and decreasing their availability to crops (Sadiq, 1997). The mass fractions of both elements were similar to those found in the literature for corn crops with the ranges of 96.7 mg kg⁻¹ to 3487.5 mg kg⁻¹ for Fe and 2.61 mg kg⁻¹ to 936.77 mg kg⁻¹ for Mn.

3.2. Total arsenic and arsenic species in the corn plant

Table 4 shows the contents of total arsenic and arsenic species in the different parts of the corn plant.

Table 4. Mass fractions (mg kg⁻¹) of arsenic content of maize plant (*Zea mays* L.) ($\bar{x} \pm SD$)

	¹ As _T	² As(III)	² As(V)	² MMA	² DMA
Root	6.92±0.12	0.00430±0.00005	0.310±0.005	⁴ ND	0.044±0.001
Stem	<LOD ³	0.00160±0.00005	0.06±0.01	0.0170±0.0005	0.0280±0.0005
Leaves	5.23±0.22	0.0050±0.0002	0.20±0.02	⁴ ND	0.1600±0.0005
Grain	<LOD ³	⁴ ND	⁴ ND	⁴ ND	⁴ ND

¹As_T: Total arsenic mass fraction.

²As(III), As(V), MMA, DMA: Arsenical species extracted from plant tissues using SDS-TRIS-HCl as extraction agent.

³LOD: 0.005 mg kg⁻¹ for As_T by ICP-MS.

⁴ND: No detected.

The highest values of the mass fraction of total arsenic were found in the roots and leaves. In the stem and in the grain, it was below the detection limit (0.005 mg kg⁻¹). This data indicates that there is no accumulation of arsenic in the grain of the corn plant. This is important since the grain is the part that is used for human consumption. In contrast, arsenic concentrations in the roots and leaves of the corn plant exceeded 5 mg kg⁻¹. These values are higher than those reported in the literature. Studies carried out on different corn plant varieties yielded arsenic concentrations of 2 mg kg⁻¹ (Rosas Castor *et al.*, 2014). Corn stems, leaves and roots are used as fodder to feed livestock. If animals consume foods with high arsenic contents, they can accumulate it and transfer it to other members of the food chain. Ultimately, this can pose a risk to humans. In the region, corn is stored through silage, which is a process of anaerobic fermentation of soluble carbohydrates in the forage to produce lactic acid. This process allows the forage to be stored during harvest time for later use in times of scarcity, maintaining the nutritional characteristics of the plants. In countries where silage is widely used, such as the Netherlands, Germany, Denmark and Switzerland, the maximum arsenic concentration allowed in silage plants is regulated. For example, in Switzerland the maximum tolerable value is 4 mg kg⁻¹ (Gulz *et al.*, 2005). The arsenic values found in the leaves exceeded this limit.

The arsenic species present in the plants were quantified from the peaks obtained by HPLC-ICP-MS. In this case, SDS-Tris-HCl was used as the extraction agent, this solution made possible to break down the organic structures of the sample and extract the different elements without interconversion of arsenic species. Four arsenic species were identified in the plants: the inorganic species As(III) and As(V), and the methylated species MMA and DMA. On the stems, all the described species were present, while in the roots and leaves, the presence of MMA was not detected. The dominant species was the inorganic As(V) being lower in the leaves and stems with 0.20 and 0.31 mg kg⁻¹ respectively. On the contrary, As(III) was always found as a minority species. Finally, The DMA species was found in higher concentration in the leaves compared to the roots.

3.3. Accumulation and translocation of arsenic in the corn plant

To quantify the capacity of the plants to absorb the toxicant, the bioaccumulation index (BAI) was calculated, which relates the concentration of arsenic in the root of

the plant to the concentration of arsenic in the soil and rhizospheric soil using the following formula (Kabata Pendias, 2004):

$$BAI = \frac{[As]_{\text{root}}}{[AsT]_{\text{soil}}} \quad (1)$$

As shown in Table 5, the quotient between the total concentration of arsenic in the roots and the total concentration of arsenic in the soil and rhizospheric soil is called BAI_T.

Table 5. Bioaccumulation index and translocation index for total arsenic.

	Soil	Rhizospheric soil	Plant
BAI _T	0.90	0.82	-
BAI _D	53.2	54.9	-
T%	-	-	75.6%

As can be seen, the BAI_T value was less than 1, this indicates that the plants roots have a low uptake of the total arsenic present in the soil. Other authors have reported BAI_T values ranging from 0.04 to 8.01 (Rosas Castor *et al.*, 2014), and from 0.8 to 2.5 (Gulz *et al.*, 2005). A more realistic scenario is to relate the bioabsorption of arsenic in the roots of the corn plant to the phytoavailable arsenic in the soil. The BAI_D values were greater than 1. This shows that the plants have a high capacity to absorb phytoavailable arsenic. The ability to absorb arsenic in high concentration is related to the nutritional status of the plant. Faced with nutrient deficiency, the plant seeks to supply its nutritional needs by increasing the absorption of different elements from the soil. If the concentration of one of the main nutrients, such as P, is low at the rhizospheric level, roots cells increase their uptake. Arsenic(V) uses the same membrane transporters as P(V), therefore, the entry of arsenic into the roots is equally favored (Zhao *et al.*, 2010). In the analyzed samples, the inorganic P content in soil and rhizospheric soil was in the order of 1000 to 1600 mg.kg⁻¹ (Table 3) with a low proportion (0.3 and 0.5% in soil and rhizospheric soil, respectively) passing to the aqueous phase. This could explain the high incorporation of available arsenic by the plant. Gulz *et al.* (2005) carried out arsenic uptake studies in corn crops under conditions of low P availability. In this situation, there was a secretion of organic acids that decrease the pH of the rhizospheric soil, which favors the increase in the availability of soil inorganic P and that of As(V).

To evaluate the distribution of arsenic in the plant, the percentage translocation was calculated using the following formula:

$$T\% = \frac{[As]_{\text{leaf}}}{[As]_{\text{root}}} \cdot 100 \quad (2)$$

The T% value is also shown in Table 5. In the samples analyzed the value greater than 70%, which indicates that the analyzed plants transport arsenic from the roots to the leaves in high proportion. Other studies in corn crops have reported T% values lower than those obtained in this study. Ranges between 0.33 to 66.5% (Sadee *et al.*, 2016) and between 0.4 to 4.7% (Gulz *et al.*, 2005) as well as values of 1.4% (Fellet *et al.*, 2007), 1.6% (Schulz *et al.*, 2007) and 20.1% (Baig *et al.*, 2010). In the plant, arsenic translocation is carried out through the xylem conductive system. Some plants, such as

the rice plant, limit arsenic transport to their aerial parts as a protective mechanism, with the aim of preventing the contaminant from reaching younger tissues (Zhao *et al.*, 2010). Uroic *et al.* (2012) studied the ability of the xylem conductive system to modify arsenic transport according to the dominant soil species. When the dominant species in the soil is inorganic arsenic, its transport to the leaf is decreased to protect the photosynthetic organ from its presence. When the methylated form is dominant in the soil, the conduction capacity of the xylem is not modified. In this sense, it is important to quantify the arsenic species present in agricultural soil and plant tissues.

In this study, no phytoavailable organic species were detected at soil or rhizospheric soil level, although they were found in the roots. This would indicate that the corn plants were capable of absorbing inorganic arsenic and storing it in methylated form. There is no consensus about the mechanism by which this methylation process could take place. However, some proteomic studies carried out in different plant species, including corn, suggest that this methylation process is the result of a joint action between rhizospheric microorganisms, endophytic bacteria and plant metabolism (Bentley and Chasteen, 2002, Requejo and Tena, 2006, Zhao *et al.*, 2010). This would explain the presence of methylated species at root level when they are not detected in the rhizospheric soil.

The inorganic species As(V) is dominant in the plant and soil compared to As(III) and the organic species. However, the presence of As(III) was detected in the roots, and a similar situation occurred with the organic species analyzed above. Requejo and Tena (2006) explain that specific reduction of As(V) to As(III) occurs in the corn root by a protein-mediated detoxification process. The As(III) obtained is stored in vacuoles as As-phytochelatin complexes, thus reducing its toxicity and preventing its circulation through the plant.

4. Conclusion

In this study, the presence and accumulation of arsenic in corn plants has been analyzed to assess the potential health risk posed by its consumption. These corn plants were grown in a geographical area with high concentrations of this metalloid in its groundwater supplies. However, arsenic was differentially distributed in the different parts of the plant evaluated, as well as in the rhizosphere soil. While arsenic was not detected in the cob kernels, high concentrations of arsenic were found in the roots and leaves of the corn plants. The corn plants showed a high capacity to absorb this phytoavailable arsenic. The dominant arsenic species in the plant-soil system was As(V). Methylated arsenic species were able to be quantified in the different plant tissues even though they were not detected in the soil. This would indicate that the plant is able to absorb arsenic in its inorganic form, translocate it and store it in organic forms, which is less toxic for the plant.

Acknowledgements

This work was supported by the Secretaría de Ciencia y Técnica de la Universidad Nacional de Tucumán within the framework of the PIUNT D632 and D754 projects.

References

- [1] Anawar, H.M., García Sanchez, A., Santa Regina, I. 2008. Evaluation of various chemical extraction methods to estimate plant-available arsenic in mine soils. *Chemosphere* 70 (8): 1459-1467. <https://doi.org/10.1016/j.chemosphere.2007.08.058>
- [2] APHA, AWWA, WPCF. 1992. Standard methods for the examination of water and wastewater. Baird, R. and Bridgewater, L. Washington, D.C.
- [3] Baig, J., Kazi, T., Shah, A., Arain, M., Afridi, H., Khan, S., Kandhro, G., Naeemullah, Soomro, A. 2010. Evaluating the accumulation of arsenic in maize (*Zea mays* L.) plants from its growing media by cloud point extraction. *Fd Chem Toxic* 48: 3051–3057. <https://doi.org/10.1016/j.fct.2010.07.043>
- [4] Bentley, R., Chasteen, T.G. 2002. Microbial methylation of metalloids: arsenic, antimony, and bismuth. *Microbiol. Mol. Biol. Rev.* 66 (2): 250–271. <https://doi.org/10.1128/MMBR.66.2.250-271.2002>
- [5] EPA. Environmental Protection Agency of U.S. 2012. Retrieved April 26th 2022, from <https://www.epa.gov/regulatory-information-topic>
- [6] Fellet, G., Marchiol, L., Perosa, D., Zerbi, G. 2007. The application of phytoremediation technology in a soil contaminated by pyrite cinders. *Ecol Eng*, 31: 207–214. <https://doi.org/10.1016/j.ecoleng.2007.06.011>
- [7] Galindo, M.C., Vece, M.B., Perondi, M.E., Monserrat Aráoz, M., García, G., Hidalgo, M.V., Apella, M.C., Blesa, M.A. 2000. Chemical behavior of the Salí River, province of Tucumán, Argentina. *Environ Geol* 40: 847-852. <https://doi.org/10.1007/s002540100243>
- [8] García, M.G., Fernández, D.S., Del Valle Hidalgo, M., Blesa, M.Á. 2000. Arsenic in groundwaters of the southeast of Tucumán province, Argentina. In: Oliver Sililo et al., (Eds), *Groundwater, Past Achievements and Future Challenges*, Balkema: 503-508. ISBN 90-5809-159-7.
- [9] Gulz, P.A., Gupta, S.K., Schulin, R. 2005. Arsenic accumulation of common plants from contaminated soils. *Plant Soil*, 272: 337–347. <https://doi.org/10.1007/s11104-004-5960-z>
- [10] IARC. 2012. Arsenic, metals, fibers and dusts. A review of human carcinogens. Vol 100C. Lyon. France. Ed International Agency for Research on Cancer. ISBN 978-92-832-1320 8
- [11] Jedinak, L., Kowalska, J., Harasimowicz, J., Golimowski, J. 2009. Speciation analysis of arsenic in terrestrial plants from arsenic contaminated area. *Sci Total Environ* 407 (2): 945-952. <https://doi.org/10.1016/j.scitotenv.2008.09.027>
- [12] Kabata Pendias, A. 2004. Soil plant transfer of trace elements. An environmental issue. *Geoderma*, 122: 143-149. <https://doi.org/10.1016/j.geoderma.2004.01.004>
- [13] Kachenko, A.G., Gräfe, M., Singh, B., Heald, S.M. 2010. Arsenic speciation in tissues of the hyperaccumulator *P. calomelanos* var. *austroamericana* using X-ray Absorption Spectroscopy. *Environ Sci Technol*, 44: 4735-4740. <https://doi.org/10.1021/es1005237>
- [14] Lin, H.T., Wang, M.C., Li, G.C. 2004. Complexation of arsenate with humic substance in water extract of Compost. *Chemosphere*, 56(11): 1105–1112. <https://doi.org/10.1016/j.chemosphere.2004.05.018>
- [15] Marwa, E.M.M., Meharg, A.A., Rice, C.M. 2012. Risk assessment of potentially toxic elements in agricultural soils and maize tissues from selected districts in Tanzania. *Sci Total Environ* 416: 180-186. <https://doi.org/10.1016/j.scitotenv.2011.11.089>
- [16] Maizel, D., Balverdi, P., Rosen, B., Sales, A., Ferrero, M. 2018. Arsenic hyper tolerant and reducing bacteria isolated from wells in Tucumán, Argentina. *Can J Microbiol.* <https://doi.org/10.1139/cjm-2017-0535>
- [17] Martínez Sánchez, M.J., Martínez López, S., García Lorenzo, M.L., Martínez Martínez, L.B., Pérez Sirvent, C. 2011. Evaluation of arsenic in soils and plant uptake using various chemical extraction methods in soils affected by old mining activities. *Geoderma* 160: 535-541. <https://doi.org/10.1016/j.geoderma.2010.11.001>
- [18] Meharg, A., Hartley-Whitaker, J. 2002. Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. *New Phytol* 154: 29–43. <https://doi.org/10.1046/j.1469-8137.2002.00363.x>

- [19] Neira, J., Ortiz, M., Morales, L., Acevedo, E. 2015. Oxygen diffusion in soils: Understanding the factors and processes needed for modeling. *J. Agric. Res.* 75: 35-44. <https://doi.org/10.4067/S0718-58392015000300005>
- [20] Nicolli, H.B., García, J.W., Falcón, C.M., Smedley, P.L. 2012. Mobilization of arsenic and other trace elements of health concern in groundwater from the Salí River Basin, Tucumán Province, Argentina. *Environ Geochem Health* 34: 251-262. <https://doi.org/10.1007/s10653-011-9429-8>.
- [21] Norton, G.J., Pinson, S.R.M., Alexander, J., McKay, S., Hansen, H., Duan, G.L., Islam, M.R., Islam, S., Stroud, J.L., Zhao, F.J., McGrath, S.P., Zhu, Y.G., Lahner, B., Yakubova, E., Guerinot, M.L., Tarpley, L., Eizenga, G.C., Salt, D.E., Meharg, A., Price, A.H. 2012. Variation in grain arsenic assessed in a diverse panel of rice (*Oryza sativa*) grown in multiple sites. *New Phytol.* 193 (3): 650–664. <https://doi.org/10.1111/j.1469-8137.2011.03983.x>
- [22] Punshon, T., Jackson, B., Meharg, A., Warczak, T., Scheckel, K., Guerinot, M. 2017. Understanding arsenic dynamics in agronomic systems to predict and prevent uptake by crop plants. *Sci Total Environ.* <https://doi.org/10.1016/j.scitotenv.2016.12.111>
- [23] Requejo, R., Tena, M. 2006. Maize response to acute arsenic toxicity as revealed by proteome analysis of plant shoots. *Proteomics* 6: 156–162. <https://doi.org/10.1002/pmic.200500381>
- [24] Rosas Castor, J.M., Guzmán-Mar, J.L., Hernández Ramírez, M.A., Garza-González, M.T., Hinojosa-Reyes, L. 2014. Arsenic accumulation in maize crop (*Zea mays*): A review. *Sci Total Environ*, 488-489: 176-187. <https://doi.org/10.1016/j.scitotenv.2014.04.075>
- [25] Ruíz Huerta, E. A., De la Garza Varela, A., Gómez-Bernal, J. M., Castillo, F., Avalos-Borja, M., SenGupta, B., Martínez Villegas, N. 2017. Arsenic contamination in irrigation water, agricultural soil and maize crop from an abandoned smelter site in Matehuala, Mexico. *J Hazard Mater*, 339: 330–339. <https://doi.org/10.1016/j.jhazmat.2017.06.041>
- [26] Ruttens, A., Cheyns, K., Blanpain, A.C., De Temmerman, L., Waegeneers, N. 2018. Arsenic speciation in food in Belgium. Part 2: cereals and cereal products. *Food Chem Toxicol*, 118: 32–41. <https://doi.org/10.1016/j.fct.2018.04.040>
- [27] Sadiq, M. 1997. Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. *Water Air Soil Pollut.* 93: 117-136. <https://doi.org/10.1007/BF02404751>
- [28] Sadee, B.A., Foulkes, M.E., Hill, S.J. 2016. A study of arsenic speciation in soil, irrigation water and plant tissue. A case study of the broad bean plant, *Vicia faba*. *Food Chem* 210: 362-370. <https://doi.org/10.1016/j.foochem.2016.04.066>
- [29] Schulz, H., Härtling, S., Tanneberg, H. 2008. The identification and quantification of arsenic induced phytochelatin comparison between plants with varying As sensitivities. *Plant soil*, 303: 275-287. <https://doi.org/10.1007/s11104-007-9507-y>
- [30] Su, Y.H., McGrath, S.P., Zhao, F.J. 2009. Rice is more efficient in arsenite uptake and translocation than wheat and barley. *Plant Soil*, 328: 27-34. <https://doi.org/10.1007/s11104-009-0074-2>
- [31] Tiwari, Y.K., Yadav, S.K. 2019. High Temperature Stress Tolerance in Maize (*Zea mays* L.): Physiological and Molecular Mechanisms. *J.Plant Biol.* 62: 93-102. <https://doi.org/10.1007/s12374-018-0350-x>
- [32] Tóth, G., Hermann, T., Da Silva, M.R., Montanarella, L. 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. *Environ Int*, 88: 299-309. <https://doi.org/10.1016/j.envint.2015.12.017>
- [33] Uroic, M.K., Salaün, P., Raab, A., Feldmann, J. 2012. Arsenate impact on the metabolite profile, production, and arsenic loading of xylem sap in cucumbers (*Cucumis sativus* L.). *Front Phys.* 3: 23-55. <https://doi.org/10.3389/fphys.2012.00055>
- [34] Ursitti, F., Vanderlinden, L., Watson, R., Campbell, M. 2004. Assessing and managing exposure from arsenic in CCa-treated wood play structures. *Can J Public Health.* 95 (6): 429-433. <https://doi.org/10.1007/BF03403987>

- [35] Wang, S., Mulligan, C.N. 2006. Occurrence of arsenic contamination in Canada: sources, behavior and distribution. *Sci Total Environ* 366: 701-721. <https://doi.org/10.1016/j.scitotenv.2005.09.005>
- [36] Yañez, M.L., Alfaro, J.A., Avila Carreras, N.M.E., Bovi Mitre, G. 2019. Arsenic accumulation in lettuce (*Lactuca sativa* L.) and broad bean (*Vicia faba* L.) crops and its potential risk for human consumption. *Heliyon* 5(1) e01152. <https://doi.org/10.1016/j.heliyon.2019.e01152>
- [37] Zhao, F.J., McGrath, S.P., Meharg, A.A. 2010. Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. *Annu Rev Plant Biol* 61: 535-559. <https://doi.org/10.1146/annurev-arplant-042809-112152>