



Spatio-temporal groundwater arsenic distribution in Central Mexico: implications in accumulation of arsenic in barley (*Hordeum vulgare* L.) agrosystem

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Abstract

In the present work, a spatio-temporal study of arsenic (As) concentration in groundwater and its impact in barley uptake is presented. The impact of As on barley is studied through the determination of its bioaccumulation in the soil-plant system, As uptake, as well as a correlation between As concentration in water and its temperature in the groundwater. For the groundwater, spatial and temporal variability of As concentration in central Mexico was determined through a geostatistical analysis using ordinary kriging. The results show that the variability of As in the ground water is correlated with its temperature ($R^2 > 0.83$). The As accumulation in the structures of plant follows the order root > leaf > ear in concentration. The bioaccumulation factor BAF_T suggests that As is mobilized to the aerial parts of the barely for both As concentrations used in the irrigation water. However, for As concentration lower than $25 \mu\text{g L}^{-1}$, the BAF_T is lower than 0.57, suggesting that the amount of As in root is the same as that contained in the aerial parts; whereas, for higher As concentrations (from 170 to $250 \mu\text{g L}^{-1}$), the BAF_T is around 0.92, indicating that the As is mainly contained in root. The spatial distribution of As concentration trend in groundwaters along the time is the same, which means high As concentration areas remain in the same groundwaters and these areas are presenting the highest water temperature. These results shall contribute to understand the bioaccumulation of As in barley and the As spatial variability in central Mexico.

Keywords Arsenic · Bioaccumulation · Ordinary kriging

Nomenclature

AME Absolute mean error
 As-DW As disposable in water

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As-TDW	As water extractable
As-TP	Total As extractable in soil
BAF_T	Bioaccumulation factor total
BAF_{TWE}	Bioaccumulation factor water extractable
TF	Translocation factor
CA	Cropland A
CB	Cropland B
D.O.F.	Official Journal of the Federation
EC	Electric conductivity
Eh	Redox potential
FAO	Food and Agricultural Organization
FVTM	Transmexican Volcanic Belt
QA/QC	Quality assurance/quality control
ME	Mean rror
NMX	Mexican norm
NOM	Mexican Official Norm
OK	Ordinary kriging
OM	Organic matter
P-DW	Phosphorous disposable in water

RMSE	Root mean square error
RMSSE	Root mean square standardized error
SCFI	Trading agency and Industrial encouragement
SEMARNAT	Mexican Natural Resources and Environmental Agency
SGM	Mexican Geological Service
SSA	Mexican Health Agency
T-As	Total arsenic
U.S. EPA	United States Environmental Protection Agency
WHO	World Health Organization

Introduction

The high levels of arsenic (As) found in groundwater and soil have become a worldwide problem. In Mexico, the presence of high levels of As in water is an active area of research, since it can be mobilized from soil to groundwater (Saldaña-Robles et al. 2018a). The World Health Organization (WHO 2008) guidelines established a maximum value of $10 \mu\text{g L}^{-1}$ for human consumption. The value allowed for As by the Mexican guidelines NOM-127-SSA (D.O.F. 1994) is $25 \mu\text{g L}^{-1}$ for As in drinking water. The Food and Agricultural Organization (FAO) as well as the WHO guidelines, established that the tolerable weekly intake, cannot exceed $15 \mu\text{g}$ of inorganic As kg^{-1} of body weight (FAO/WHO 2011a, b). Thus, the high concentrations of As found worldwide has motivated an intense research activity on the implications of the presence of As in agrosystems and its impact in human health (Castor et al. 2016; Núñez et al. 2016; Saldaña-Robles et al. 2018b).

Particularly, in central Mexico (located in the Transmexican Volcanic Belt, FVTM) high As concentrations are found naturally, and it is easily mobilized due to geological and geomorphological features (Saldaña-Robles et al. 2018b). A previous study reports that As concentration in groundwater ranges from 25 to $120 \mu\text{g L}^{-1}$ in the northern Guanajuato (Ortega-Guerrero 2009), whereas the As concentrations found in groundwater used for irrigation in central Mexico ranges from 40 to $200 \mu\text{g L}^{-1}$ (Zanor et al. 2019). On the other hand, Morales et al. (2015) indicated that As contents in groundwater is related to the presence of rhyolite units as main rocks in the aquifers and the circulation of geothermal water which reach temperatures up to 50°C could help to mobilize the As. However, very little research has been done to study the sources, mobilization, as well as the spatio-temporal distribution of As in central Mexico.

The mobilization mechanisms are important to understand, since humans are exposed to As through food consumption coming from water-soil-crop system (Praveen et al. 2017). Thus, although As could be found at low concentrations in food,

several governmental agencies, such as the European Food and Safety Authority, have stressed the risks that this metalloid represents to human health (Moreno-Jiménez et al. 2016).

Agriculture is the most consuming water activity and thus it is important to understand at which level mobilizes As from irrigation water to the crops through its root. Some authors address that those specific mechanisms deserve a detailed study (Dahal et al. 2008; Marques et al. 2009; Rothwell et al. 2009; Morales et al. 2015). Furthermore, different human practices such as, inadequate practices in agricultural activities, irrigation using deep waters, pesticides, and contaminated residual water tend to increase the As concentration in the water-soil-cultivation system (Vamerali et al. 2009; Zhao et al. 2009).

Rice is a widely studied crop, where the uptake, translocation, and accumulation mechanisms has been extensively studied (Meharg and Jardine 2003; Raab et al. 2007; Lemos-Batista et al. 2014; Praveen et al. 2017), from the distribution of inorganic and organic As in rice grains (Meharg et al. 2008; Lombi et al. 2009; Carey et al. 2012) to the speciation analysis, daily intake estimations (Batista et al. 2011), and the determination of As according to the origin and type of rice (Sommella et al. 2013; Segura et al. 2016).

The As accumulation in plants leads to the transfer of this metalloid from soil to the food chain. Indeed, due to the chemical similitude of the inorganic As(V) found in the oxic layer of soil with phosphate, As accumulation in plants occurs through the phosphate transporter system, where it is converted to As(III). The highest As concentration in plant is found in root, and this result is due to the competition mechanisms between As and P (Mayorga et al. 2013; Sadee et al. 2016; Zvobgo et al. 2018).

The spatial and temporal distribution of As concentration is also an important aspect to take into consideration. Hossain and Bagtzoglou (2007) considered geo-spatial-generated information as a clue practice to manage the contamination in developing countries where detailed information is not available. In fact, kriging interpolators and its variants are widely used as tools to study the spatial and temporal distribution of As concentration (Daya and Bejari 2015; Zahid et al. 2015; Sabet-Aghlidi et al. 2018). Thus, geostatistics prediction of spatial and temporal distribution of contaminants employed to find trends, replaces an intensive sampling methodology (Sabet-Aghlidi et al. 2018).

In central Mexico, barley is one of the most important crops, and the presence of As represents a considerable risk to human health. Thus, a high As concentration in barley intensifies the As consumption by humans. The present work focuses on the following issues; (a) bioaccumulation of As in the soil-plant system, (b) spatio-temporal variability of As concentration in groundwater, in central Mexico; and (c) As uptake in barley and a correlation between As concentration and temperature found in groundwater.

Study area

The study area is located in the northern part of Irapuato city, in central Mexico (see Fig. 1). The selected zone is important for the national economy due to the high production of grains and vegetables.

The geological framework of the region is characterized by volcanic rocks, mainly composed of basalts and andesites of the Tertiary and Quaternary ages (Mexican Geological Service (SGM)). Isolated outcrops of Tertiary limestone are also recognized. The most recent sediments are dominated by alluvial and colluvial materials and soils (Nieto-Samaniego et al. 2012). Morales-Arredondo et al. (2016) show that the main source of As in near areas to the study zone is due to the minerals contained in rocks that are naturally found in the region. Thus, it is expected that the main contribution of As in soil and water are of geogenic origin, and the As is mobilized by the mining activities (Ruíz-Huerta et al. 2017).

The weather of the study area corresponds to a warm sub-humid type. The regional rainfall averages 660 mm year^{-1} and evapotranspiration reaches a total annual value of 2100 mm. The monthly mean temperature is about 19.8°C where the hottest month is May with a maximum temperature of 23.9°C (Zanor et al. 2019).

Experimental

Sampling and treatment of water, soil, and plant

Water

The groundwater wells are situated in croplands where 32 samples were collected randomly. The samples were collected during the dry and wet seasons in 2010. The soil and barley plants were collected from two agricultural croplands, labeled as cropland A (CA) and cropland B (CB). The sampling sites were selected since, (a) the cropland sites were very close to each other, and thus, the climatological and geological variations are expected to be minimal, and (b) the As content in irrigation water used in CA is less than $25 \mu\text{g L}^{-1}$ whereas the As content in CB ranges from 170 to $250 \mu\text{g L}^{-1}$.

A total of 96 samples were collected in three periods (July 2009, December 2009, and May 2010), 32 groundwater sites were sampled for each period. The groundwater samples were collected from wells (using hand pumps and boreholes) located at different depths ranging from 21 to 146 m from the Irapuato-Valle de Santiago aquifer. The samples were collected and stored in plastic sealed tubes. The pH and temperature were measured in field using a pH/EC meter (HANNA instruments) and adjusted with concentrated nitric acid at pH 2.0 to

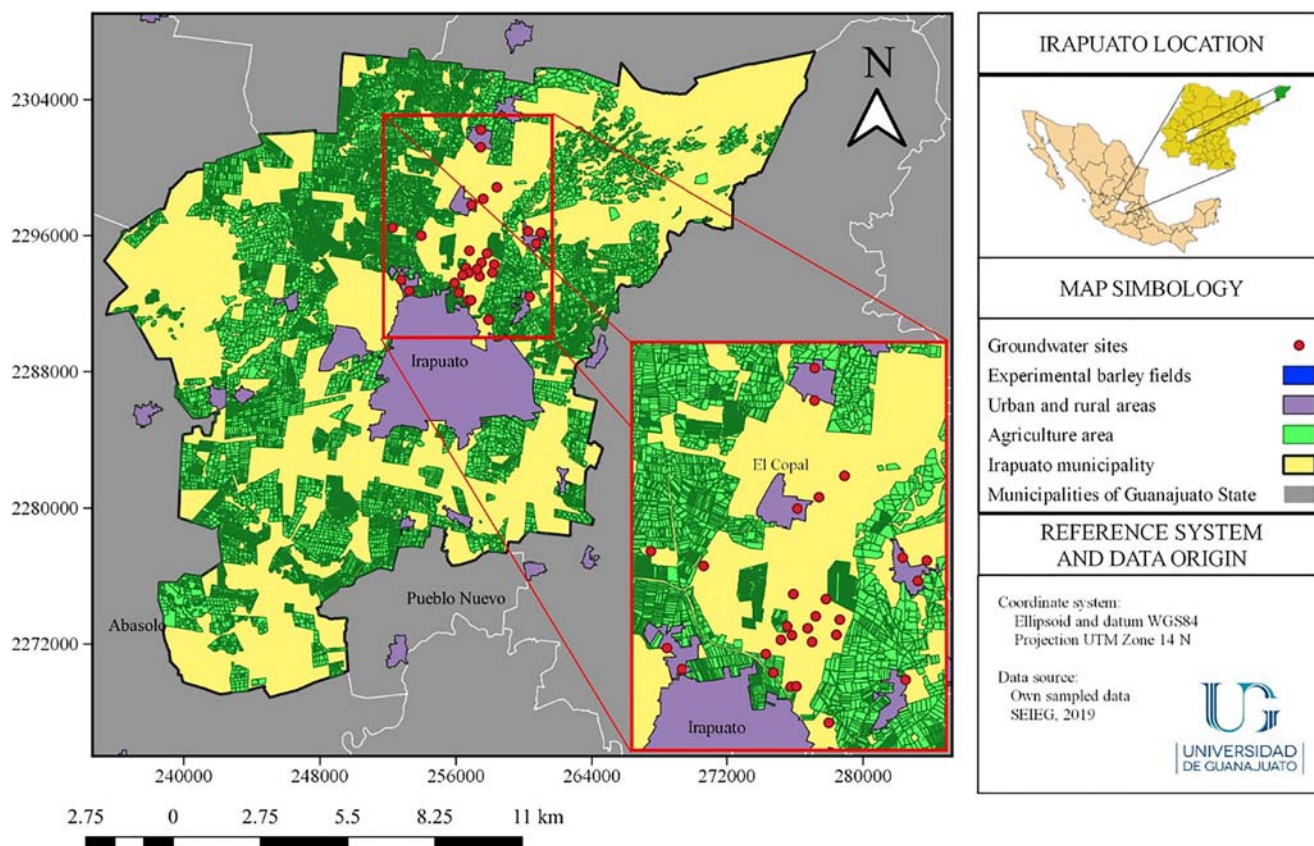


Fig. 1 Location of the study area (red dots indicate the sampling sites of the groundwater wells and soils)

preserve the sample for later chemical analysis. All samples were collected after purging for 5–10 min, filtered (Watman paper 41) in situ, and stored in 1 L plastic (propylene) bottles at 4 °C following the sampling protocols and methods defined by the Mexican guidelines NOM-014-SSA1 (D.O.F. 1993).

Soil

Soil sampling were collected following the Mexican standard NMX-AA-132-SCFI (Secretary of Economy 2016). A total of 10 sub-samples were collected at 0.30 m in deep, for each selected cropland to form a composite sample by triplicates. Two samplings were done, the former before seedtime and the later after harvest. The samples were collected with a plastic shovel and stored in a plastic bag to keep them free of metal contamination. All the soil samples were dried at room temperature for 2 weeks. The quartering method was used and then it was sieved through a < 2-mm mesh.

Barley plant

The sampling of the barley crop was methodically and systematically conducted in the two croplands sowed with a certified seed (var. Esmeralda) on 7 December 2009. The grown conditions for barley crop such as soil, weather, solar radiation, rainfall, fertilization, and irrigation were similar for each selected cereal field. However, as mentioned above, the As concentration in the irrigation water was different for each cropland.

The samples were collected from five points located with a Global Positioning System covering the whole cropland. Sampling 1 was carried out in the tiller (initial, 30 days), sampling 2 during the stem elongation (intermediate, 75 days), and sampling 3 before the harvest (ripening, 135 days). All the samples were stored in plastic bags, and crop samples were manually segregated in parts (i.e., grain husk, leaf stem, and root) of the barley plant. Each part was washed with distilled water, and then dried at 70 °C for 72 h, crushed in a mortar and sieved through a < 2-mm mesh.

Water, soil, and plant analysis

Water

The total As in the water sample is quantified using the U.S. EPA 6010C/ICP (2000) guidelines. The ICP analysis was used to determine total As content using an induction-coupled plasma atomic emission spectroscope (ICP-AES, model Iris Intrepid Thermo Elemental, Thermo Scientific Company, Waltham, MA, USA). The operating conditions employed are in accordance to the guidelines given by U.S. EPA 6010C/ICP (2000). The accuracy of the results for As determination was checked against the measurement of an internal blank and three calibration standards. For the QA/

QC, the practical limit of quantification of As was of 0.025 mg L⁻¹ and the determination method limit was of 0.0025 mg L⁻¹. As an internal quality control for the water determinations, five concentrations are used for the calibration curve. Besides, the first point of the calibration curve is selected greater or equal to the practical limit of quantification and the final point is selected to be inside the lineal interval. The correlation coefficient for the calibration curve was 0.995, and the As recovery ranges from 90 to 110%. Also, in each run, a standard addition sample was analyzed with a recovery ranging from 80 to 120%.

Soil and plant

The physical and chemical characterization of the soil samples were determined using Mexican guidelines SEMARNAT NOM-021 (2000). The Bouyucos method (Bouyucos 1962) was employed to determine the clay fraction, in which pH and EC were measured in a 1:1.2 ratio of soil:water mixture with a Conductronic PC45 potentiometer. The organic matter (OM) was determined by loss on ignition. Carbonates were determined using a Bernard calcimeter with HCl at 50% and 0.2 g of soil. Concentrations of available phosphorous were determined by colorimetry according to the Olsen method, reading in a spectrophotometer at 882 nm. All samples were analyzed in triplicates, sealed in plastic bags, and stored at - 20 °C before analysis to prevent it from chemical degradation.

The U.S. EPA 3051A (2007) guidelines were used for plant and soil digestion. The digestion for plant and soil were carried out in a microwave oven (CEM, Model MARSX 230/60). The digestion took place in two stages, with 0.5 g of homogenized sample (soil or plant) and 2.5 mL of concentrated HCl and 7.5 mL of HNO₃ (Vercoutere et al. 1995). During the first stage, the microwave oven was set to a pressure of 0.827 MPa (120 psi) at 90 °C for 15 min. In the second stage, the mixture was heated at 130 °C (reached in about 5 min) and kept for 25 min. The digested samples were cooled to room temperature and filtered (Watman paper 41).

Total As in the sample (soil and plant) was quantified with the U.S. EPA 6010C/ICP (2000) guidelines for each sample. For the soil and plant analysis, the QA/QC criteria implies a practical limit of quantitation of 10 mg kg⁻¹ whereas the determination method limit was of 1.362 mg kg⁻¹. The correlation coefficient obtained is of 0.995 with an initial verification of the calibration curve with a difference of 10% and a sample was added to each batch of 20 samples with a difference of 20%.

Data Analysis

The study of spatial and temporal distribution of As concentration was carried out for the data of As concentration

determined from groundwater samples. Each dataset obtained were used to generate a map of As spatial distribution.

Descriptive data analysis

A descriptive analysis was done for each of the three datasets of As. This analysis was done as the first step as suggested in the technical literature (Daya and Bejari 2015; Sabet-Aghlidi et al. 2018). The descriptive statistical description takes into account the mean, median, standard deviation, skewness, and kurtosis. A simple classification map showing georeferenced points and concentration levels of As by color was elaborated to observe tendencies. Also, datasets were transformed, and the experimental and theoretical variograms were established. Finally, ordinary kriging (OK) interpolator was applied to each set of data. The number of data used in the OK was 29 since three of the sampled data were unacceptable. Even that the number of data is not recommended to carry out an OK interpolation, it was done, since it provides an insight on spatial tendencies of As concentration distribution, which were also very similar to those observed in maps of classes of As concentration. After OK interpolation was carried out, a natural log back transformation and validation were carried out.

Variogram

A semivariogram is a measurement of dis-similarity between observations on a surface as a function of the distance between them. The semivariogram is required in any kriging interpolator method and it is computed as

$$\hat{\gamma}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_{i+h})] \quad (1)$$

where, $\hat{\gamma}(h)$ is the semivariance, N is the number of pairs of sampled sites at a distance h , $Z(x_i)$ is the value of a characteristic of the surface at x_i location and $Z(x_{i+h})$ is the characteristic of the surface at x_{i+h} location.

In this work, the semivariogram models were encountered by a trial-and-error approach while observing four parameters obtained from the cross-validation methodology. This methodology is mainly based on recommended literature (Li and Heap 2014).

Validation

Cross-validation is a technique that removes a data point from the available set of data and then estimating the value of the removed point. The difference between the estimated value and the measured value at the removed data point is the error estimate. This error can be viewed as a signed error, absolute

error, or standardized error. Then, indicators used as a result of cross-validation are the next error statistics; mean error (ME), absolute mean error (AME), root mean square error (RMSE), and root mean square standardized error (RMSSE). These parameters were used as indicators of the best semivariogram and quality of OK interpolation while trying for different lag sizes and lag intervals of semivariogram.

Ordinary kriging

OK is a prediction method based on the interpolation of data to estimate a spatially distributed variable. OK considers a local second-order stationarity and evaluates a mean in a moving neighborhood defined by a search radius. The OK estimator is given by

$$\hat{Z}(x_0) = \sum_{i=1}^n \lambda_i Z(x_i) \quad (2)$$

where $\hat{Z}(x_0)$ is kriging estimation at location x_0 , $Z(x_i)$ is sampled value at location x_i , and λ_i is the normalized weight factor related to $Z(x_i)$. The estimated error is described by,

$$R(x_0) = \hat{Z}(x_0) - Z(x_0) \quad (3)$$

where, $Z(x_0)$ is unknown true value at x_0 and $R(x_0)$ is estimated error. Since OK is an unbiased estimator, the mean error must equal zero. The mean error is determined as

$$ME \{R(x_0)\} = 0. \quad (4)$$

More details of OK applications for ground spatially distributed water variables can be found in the technical literature (Shieh et al. 2005; Yamamoto 2005). The software used in this study was SADA 5.0.7800.0.

Bioaccumulation and translocation factors

The bioaccumulation factor as well as the translocation factor are used to study the mobilization of As in the parts of the plant (Rosas-Castor et al. 2014). The bioaccumulation factor is defined as the ratio of the total As concentration in root over the total As concentration in soil (BAF_T). This is

$$BAF_T = \frac{[As_{Troot}]}{[As_{Tsoil}]} \quad (5)$$

The BAF_{TWE} is defined as total As concentration in root over the total As concentration in water extractable of soil and is determined as

$$BAF_{TWE} = \frac{[As_{Troot}]}{[As_{TDWsoil}]} \quad (6)$$

Finally, the translocation factor is defined as the percentage of the As concentration in stem and leaves over the As

concentration of As in roots is the translocation factor (TF). This is determined

$$TF = \frac{[As_{Taerialpart}]}{[As_{Troot}]} \quad (7)$$

Results and discussions

Water characterization and geostatistical analysis

As concentration at groundwater samples

Basic statistical summary Table 1 shows a basic statistical summary of As concentrations in water at sampled groundwater sites for three different dates. The lowest mean of As concentration was found in July 2009 ($71.3 \mu\text{g L}^{-1}$), intermediate mean in December 2009, and the highest in May 2010 ($129.1 \mu\text{g L}^{-1}$). Also, the lowest median of $41 \mu\text{g L}^{-1}$ of As was found in July 2009, which is lower than the mean of the same date. The same behavior was found for December 2009 and May 2010. Medians per date were smaller than corresponding means, which implies a positive skewness obtained for the three datasets. The positive skewness indicates that more groundwater sites presented low As concentration values than those with high concentrations. Additionally, kurtosis coefficient was lower than 3 (normal distribution) for July 2009 data, which can be interpreted as the right tail heaviness of the distribution. It means that some high atypical As concentrations at certain sampled locations. Kurtosis was higher than 3 for December 2009 and May 2010, and the As concentration increased from July 2009 to May 2010. By comparing maximum detected and mean-standard deviation of As concentration for each date, atypical high values can be corroborated (see Table 1).

Semivariogram of As concentration and cross-validation

Table 2 shows the spherical models chose to interpolate the variability of data. Model parameters for July 2009 dataset were different from those found for December 2009 and

May 2010, which were similar. ME which is close to zero showed that the chosen models for the three datasets of As concentration were balanced in the sense that As concentrations were as much overestimated in some sites as they were underestimated in other sites. In July 2009 and May 2010, the As concentrations were slightly over-estimated ($ME > 0$) and December 2009 values were underestimated ($ME < 0$). Ideally, absolute mean error should be zero, indicating that predicted values are identical to sampled data and for this study the AME showed values of 81.58, 122.26, and 83.77 for July 2009, December 2009, and May 2010. These results indicated a poor performance of the theoretical model, since these numbers represent an important percentage of original data variability, when considering minimum and maximum concentrations of As for each dataset. RMSSE should be close to one when the predicted standard errors are valid, and for this study, the RMSSE values were close to one for the three datasets. July 2009 and May 2010 RMSSE values were lower than one indicating again over-estimation of original values, while December was greater than one indicating under-estimation of original sampled values. According to this analysis, the interpolated kriging maps represents fairly the variability of As concentration.

Ordinary kriging interpolation of As concentration After the best theoretical models were obtained, the OK interpolation was carried for all datasets of As concentrations at each date, and the results are shown in Fig. 2.

The three maps show a very remarkable division of two areas, namely low and high As concentration areas. The west area presents a high As concentration trend, while the east presents low As concentration trend. In July 2009, the As concentrations were zero or not detected due to a very low concentration. In December 2009 and May 2010, the maximum As concentration found are $520 \mu\text{g L}^{-1}$ and $510 \mu\text{g L}^{-1}$, respectively. On the other hand, an increase of As concentration in water can be observed from July 2009 to December 2009, and it occurs at both low and high As concentration areas. However, the trend of As concentration in May 2010 remains similar to December 2009 with just a slight increase in some sites of the low concentrations area.

Table 1 Univariate analysis of As concentrations at groundwater well sites

Sampling date	Sampled groundwater	As concentration ($\mu\text{g L}^{-1}$)						
		Mean	Median	Standard deviation	Skewness	Kurtosis	Min detect	Max detect
July 2009	29	71.3	41	86.1	1.12	0.32	b.d.l.	290
Dec 2009	29	108.0	72.5	117.9	1.78	4.14	8	520
May 2010	29	129.1	73	158.7	2.24	6.02	8.6	510

b.d.l., below detection limit

Table 2 Theoretical model of semivariogram and cross-validation results of OK interpolation for As concentration

Sampling date	Model	Nugget effect	Sill	Major range	ME	RMSE	AME	RMSSE
July 2009	Spherical	1500	9030	2100	0.0589	81.58	63.05	0.9456
Dec 2009	Spherical	0	21,070	2500	-0.2467	122.26	73.75	1.2076
May 2010	Spherical	0	22,390	2205	0.5293	83.77	60.68	0.8814

Temperature at groundwater samples

Basic statistical summary A basic statistical summary of water temperatures at groundwater sampled sites is presented in Table 3. The minimum mean temperature was found in December 2009, the intermediate mean temperature was found in May 2010, and the maximum mean temperature was presented in July 2009. The median temperature in July 2009 was almost the same as the median temperature in December 2009, while the lowest median was found in May 2010. Skewness was small (below 0.20) and kurtosis was lowest in July 2009. The maximum detected temperature

for the three dates was 45 °C, and the minimum was 18 °C for December 2009 and May 2010. The three datasets presented a negative kurtosis indicating heavily tailed distributions.

Semivariogram of temperature at sampled water wells

Table 4 shows the theoretical model parameters chosen to yield the best cross-validation indicators. Spherical models were used for the three datasets and model parameters were different between the three datasets.

ME showed a value close to zero indicating a good balance between over and underestimated values for all datasets, and December 2009 and May 2010 ME values were positive

Fig. 2 Spatial distribution of As concentration by OK interpolator at sampled sites of water wells. **a** July 2009; **b** December 2009; **c** May 2010

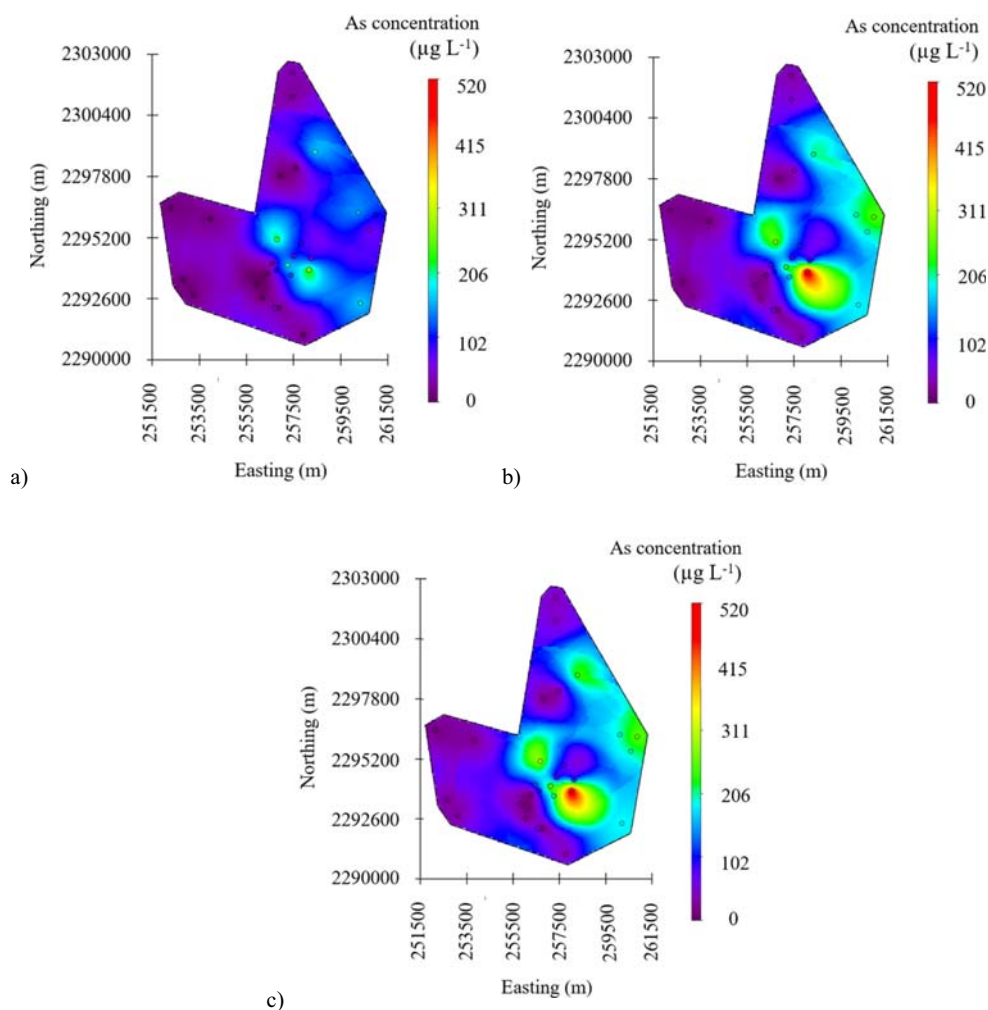


Table 3 Univariate analysis of water temperature at sampled sites

Sampling date	Number of sampled sites	Water temperature (°C)						
		Mean	Median	Standard deviation	Skewness	Kurtosis	Minimum detect	Maximum detect
Jul 2009	28	33.47	32.05	7.85	0.02	− 1.46	22.00	45.00
Dec 2009	28	31.44	32.00	7.99	0.20	− 0.92	18.00	45.00
May 2010	28	32.32	30.50	7.53	0.14	− 0.94	18.00	45.00

indicating over-estimation, while July 2009 ME indicated underestimation. RMSSE confirmed overestimation for December and May and under-estimation for July 2009. AME values showed a poor model performance since its values are greater than 20% of the temperature range for each dataset. Thus, the cross-validation indicators shows that maps generated with the chose geostatistical model can fairly represent the variability temperature around the studied area.

Ordinary kriging interpolation of temperature Maps shown in Fig. 3 results by using the theoretical variogram models for temperature at the three dates and OK interpolation.

The temperature scales are the same between each map, which allows a better comparison for spatial and temporal trends. The groundwater wells located at the east side presented higher temperature than western groundwater wells of the sampled area. In July 2009 map, it can be noticed that the difference of temperature between east and west is more remarkable than for December 2009 and May 2010. In fact, May 2010 shows very little difference between temperatures at east and west water wells. Also, the spatial trend of temperature and As concentration show similarities, since east groundwater wells presented higher temperature and As concentration than those at the west and it can be easily observed in the interpolated maps of both variables. These spatial trends between temperature and As concentration of water suggest a possible condition of higher As concentrations for thermal groundwater wells.

Figure 4 presents the correlation of As concentration between pair combinations of the three periods. The correlation coefficients where 0.98, 0.84, and 0.84 for the periods July–December, July–May, and December–May, respectively, with a significance level of $P = 0.05$. The high correlation coefficients indicate that the linear model fits reasonably well for the three periods. Besides, this evidences that exists a correlation between the As concentration for any two samplings along

time. For instance, from July to December there is a higher correlation between the As concentration than in the period July 2009–May 2010. These results suggest that the As concentration is strongly correlated for shorter periods of time and its correlation diminishes in the subsequent months.

In addition, the goodness of fit is evaluated through the standardized residuals, which are defined as the ratio of the residuals of the estimated variance and the lack of fit test. The standardized residuals ranges from − 1 to 3, suggesting that the variation between the estimated variances is not so far from the measured As concentration. In addition, the standardized residuals are randomly distributed along the x -axis, indicating that there is no significant error due to the selected model.

Figure 5 presents a non-linear correlation between the As concentration and temperature for the three samplings. The data fits reasonably well to a quadratic model and correlation coefficients of 0.83, 0.73, and 0.76 for the sampling on July 2009, December 2009, and May 2010, respectively. It is observed that the higher correlation exists for the sampling at higher temperatures. Also, these results are coherent with the spatial trend observed in temperature and As concentration in groundwater wells, this is, as higher the temperature of water, the higher As concentration of it. The correlation for the higher temperature could be related to a higher dissolution of the As contained in rocks of the groundwater.

The results show that the model fits reasonably well to the data, since its residuals are randomly distributed and the range of − 1 to 3 suggests that the variation between the estimated variances is not so far from the measured As concentration.

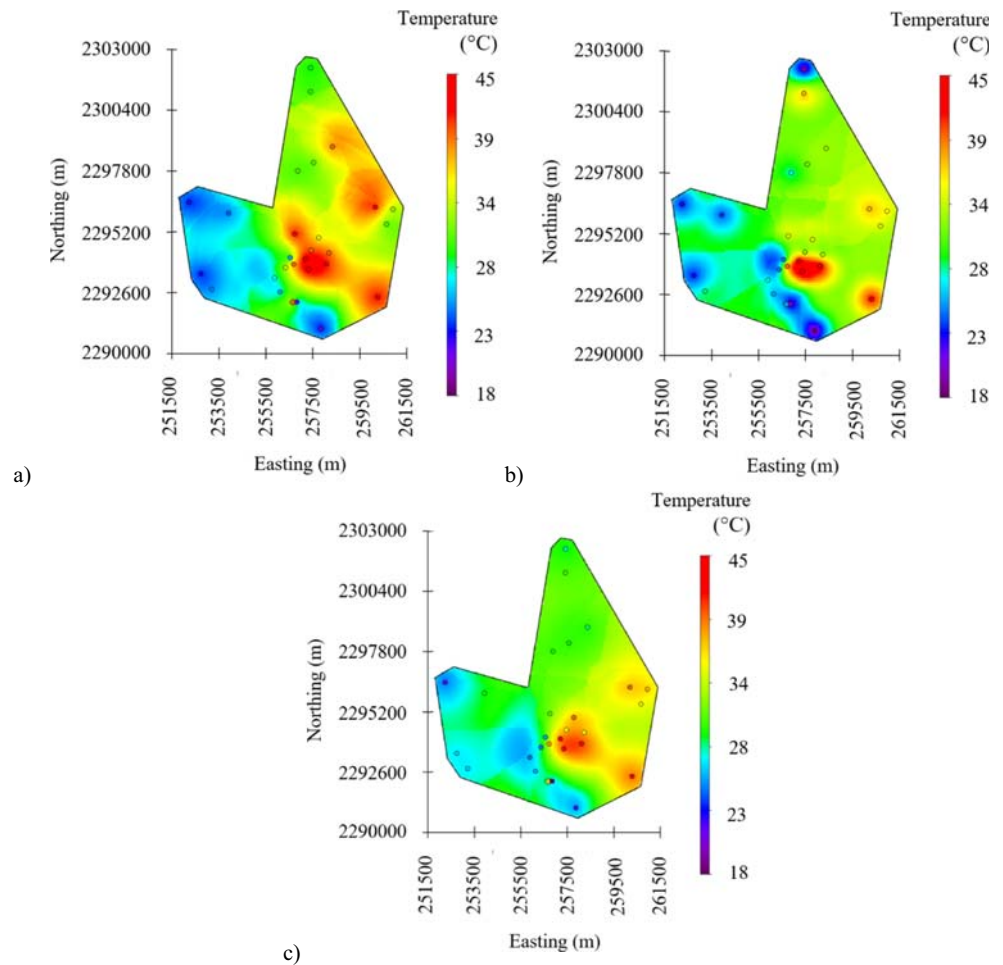
Soil

The physicochemical parameters obtained are shown in Table 5. According to its texture, the soils of the two croplands

Table 4 Theoretical model of semivariogram and cross-validation results of OK interpolation for temperature

Sampling date	Model	Nugget effect	Sill	Major range	ME	RMSE	AME	RMSSE
July 2009	Spherical	15.50	86.22	2480	− 0.21	9.53	7.39	1.16
Dec 2009	Spherical	5.77	57.31	1435	0.34	7.12	5.66	0.97
May 2010	Spherical	25.08	36.37	2579	0.17	6.47	5.06	0.93

Fig. 3 Spatial distribution of temperature by OK interpolator at sampled sites of groundwater wells. **a** July 2009; **b** December 2009; **c** May 2010



from central Mexico were classified as clayed loam (see Table 5). OM contents range from 5.71 to 6.06 mg kg⁻¹. The total As (T-As) for CA and CB ranges from 0.19 to 2.18 mg kg⁻¹, respectively. The As concentrations found in soil were under the guidelines established by the World Health Organization (WHO 1981) for As in soil (ranging from 0.2 to

40 mg As kg⁻¹). Therefore, the As concentrations in soils were lower than the determined in other studies, such as: in Guanajuato Mexico (1372 µg kg⁻¹, Saldaña-Robles et al. 2018b), in Central Mexico (2580, 7300, and 8100 µg kg⁻¹, Zanol et al. 2019), in Nawalparasi Nepal (6100 and 16,700 µg kg⁻¹, Dahal et al. 2008), and in India (up to 19,400 µg kg⁻¹,

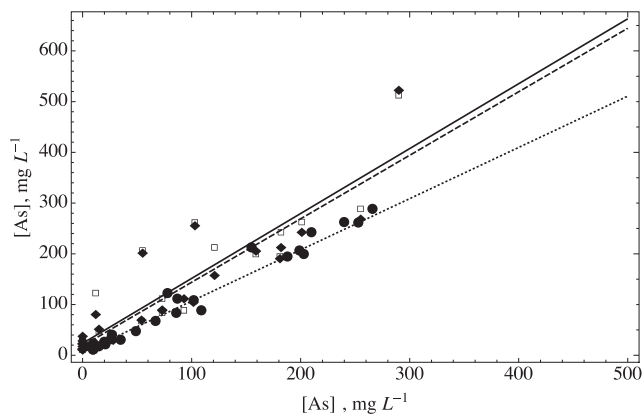


Fig. 4 Linear correlation of As concentrations of water in groundwater between July 2009 and December 2009 (filled diamonds), July 2009 and May 2010 (empty squares), and December 2009 and May 2010 (filled circles)

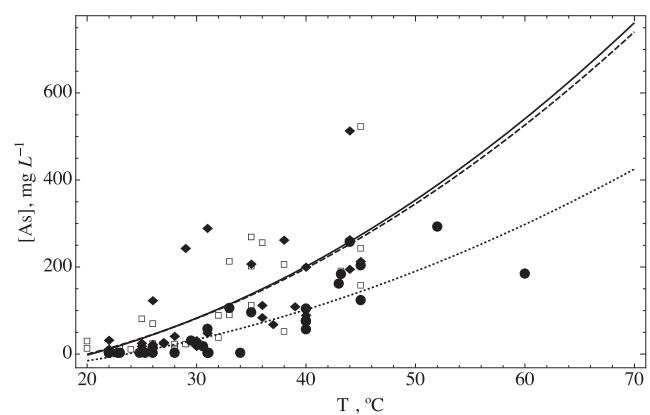


Fig. 5 Correlation of As concentration and temperature of water in groundwater at different dates. In July 2009–December 2009 (filled diamonds), July 2009–May 2010 (empty squares), and December 2009–May 2010 (filled circles)

Table 5 Physicochemical parameters for SA and SB samples

Texture	SA Clayed loam	SB Clayed loam
OM (%)	5.71	6.06
Electrical conductivity (dS m ⁻¹)	0.27	0.30
pH	8.0	8.1
Bulk density (g cm ⁻¹)	1.11	1.08
T-As (μg kg ⁻¹)	19.21	2177.17
As-DW (μg kg ⁻¹)	< 25	1560.00
P-DW (mg kg ⁻¹)	5.50	6.80
As in water irrigation (μg L ⁻¹)	< 25	170–250

Roychowdhury et al. 2005). In addition, it is found that barley accumulates As in their different structures, and the As concentration in soil was found to be correlated with the As concentration in water. These results agree with the obtained by Dahal et al. (2008), where it is shown the influence of irrigation water on As concentration found in soils.

The As disposable in water (As-DW) was below the detection limits for the CA and around 1560 μg kg⁻¹ for CB, while the phosphorous disposable in water (P-DW) was 5.5 and 6.8 mg kg⁻¹ for CA and CB, respectively; this suggests a competition between ions by adsorption in soil and sorption by plant. Previous works (Zvobgo et al. 2019) showed that phosphorous could reduce the As toxicity, resulting in a minor As concentration in the structures of barley and it is associated with the growth of the plant. The chemical similitudes between the arsenate and phosphate, indicates that phosphate can be replaced by arsenate in biomolecules like adenosine triphosphate (Punshon et al. 2017). The values of electric conductivity (EC) shown in Table 5 were very similar between CA and CB (0.27 and 0.30 dS m⁻¹), which presented a moderate salinity according to the Mexican guideliness NOM-021 (SEMARNAT 2000). The pH values were alkaline in both and very similar, this is, pH in CA was 8.0 and 8.1 for CB. The OM content was 5.71 and 6.06 % for SA and SB, respectively. According to the guidelines of Mexican NOM-021 (SEMARNAT 2000), this is a high content of OM. The OM in soil plays an important role in the availability of As, since OM influences nutrient availability, pH, and redox potential (Eh) (Gustave et al. 2017).

Plant

The total As concentration found in root is shown in Fig. 6. The barley root collected from the CB presents higher As concentrations than the root collected from the CA. The labels “sample 1,” “sample 2,” and “sample 3” represent the time sampling along the crop cycle. The total As concentration in root ranges from 1000 to 20,000 μg kg⁻¹ of dry mass for CA

and CB, respectively. These results show that a difference in irrigation water has a great impact on the As accumulation, in accordance with the results obtained by Dahal et al. (2008).

Besides, as is observed, the accumulated As in root during the three samplings for the CA is maintained relatively with no change, whereas from the first to the second samplings in the CB, there is a dramatic increase in the As accumulation. This same behavior is observed for leaf and ear for both croplands. This behavior agreed with previous works (Saldaña-Robles et al. 2018b; Carracelas et al. 2019) which showed higher As concentration in water and higher concentration in tissues. These results suggest the existence of a lower bound in As concentration which can be contained in the irrigation water which maintains the crop without increase the As bioaccumulation. However, as it is discussed in the following section, for As concentration in water below to 25 μg L⁻¹ the As is accumulated in the same concentration in all the aerial part in the same percentage than the As concentration contained in root.

Figure 6b shows that for leaf, there is an increase in the As accumulation in the CA and CB as barley growths. The same behavior is observed for ear, since the As concentration increases dramatically for both CA and CB in the third sampling. This effect can be related to the process of grain filling which occurs during the third sampling. Namely, as the ear starts to grow, the As moves from root to the leaf leaving the ear with relatively low amounts of As (lower than 100 μg kg⁻¹ dry mass for CA and around 100 μg kg⁻¹ of dry mass for CB). However, as the ear continues growing, this mechanism tends to move the As to it. These results are consistent with previous works in other crops (Farooq et al. 2016; Sharma et al. 2020), which found that once the root has absorbed the As, it is translocated to other plant tissues. During the first sampling, there is no ear, so the total As is reported as zero. For sampling dates 2 and 3, the barley starts to grow and an increase in the amount of As stored in the different tissues is observed. In Fig. 6, the greatest amount of As is found in root followed by leaf and ear in decreasing order. These results show that the root behaves as a filter of As and thus keeping low As concentrations in the ear. In a previous work (Suriyagoda et al. 2018), the concentration of As in rice grain increases when the soil As concentration increases up to 60 mg kg⁻¹ in soil. The same behavior is obtained in the present work, namely, as the concentration of As increases in soil and water, the As concentration in grain from 0 to 0.987 mg kg⁻¹, respectively, for both croplands. Finally, in this work, the As concentration found in grain was greater than that permissible for grains (< 0.2 mg As kg⁻¹), as suggested by FAO/WHO (2014).

The As is toxic for plants (Sharma 2012), although the tolerance and stress response to As concentration depends on As species, crop, and physicochemical properties of the soil among other properties (Choudhury et al. 2011). The high concentrations of As in the different structures of crops can affect growth and yield, such as in barley, rice, carrot, onion,

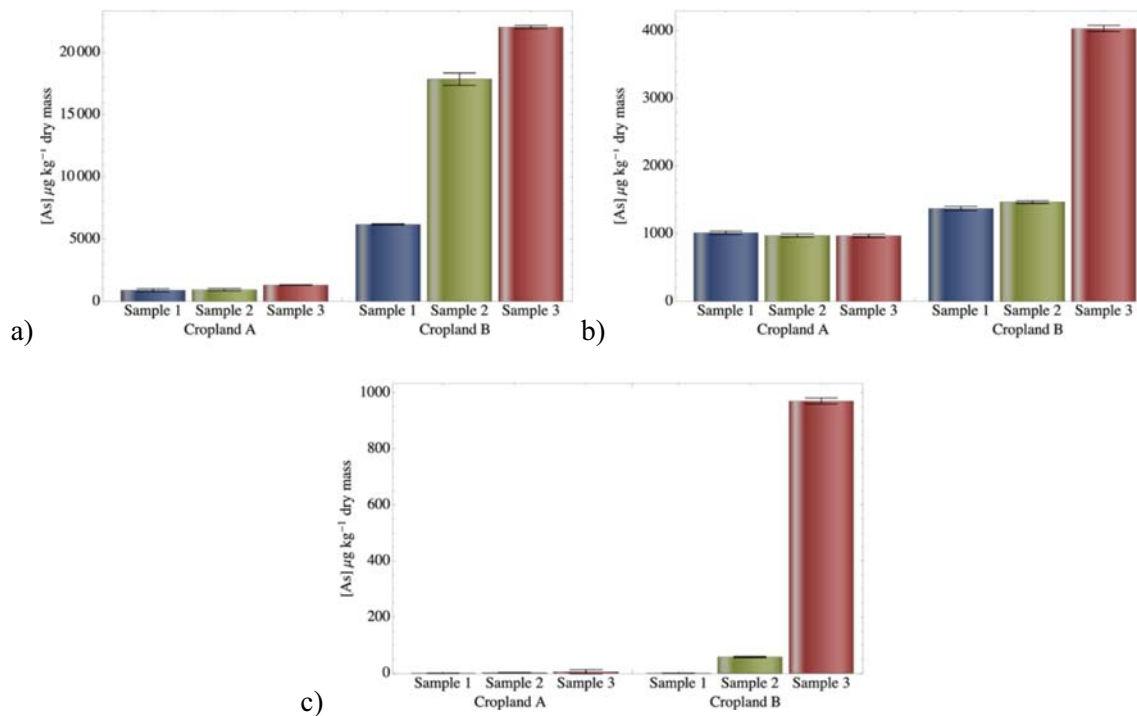


Fig. 6 Total As concentration in **a** root, **b** leaf, and **c** ear for the three samplings (bars on the top represent the standard deviation of the samples)

potato, and cauliflower (Rahman et al. 2007; Dahal et al. 2008; Mayorga et al. 2013; Saldaña-Robles et al. 2018b). Previous works (Carracelas et al. 2019) found that the yield of rice was reduced by 14% in comparison to the control case. In this study, it is found that the yield of barley was reduced by 10% for CB when compared to CA.

As it is observed in Table 6, the BAF_T is lower for CA than for CB. These results suggest that for lower concentrations of As in root, the As is distributed equally in all the parts of the plant; however, as the As concentration available in soil is increased, the As is mainly retained in the root. These results suggest that there exists a threshold, such that before it is reached, the As can move in the stem and leaf in proportional amounts to the root. Once this threshold is reached, the root acts as a natural filter for stems and leaves retaining a higher amount of As. On the other hand, the BAF_{TWE} suggests that not all the As available in water is retained by the root. Namely, for lower As concentration in the irrigation water ($[\text{As}] < 25 \mu\text{g L}^{-1}$ used in CA), the ratio of As retained by the root is higher than the ratio of As retained for higher As content ($[\text{As}]$ ranging from 170 to $250 \mu\text{g L}^{-1}$ used for CB). Thus, as the As available in water is higher, the BAF_{TWE} factor becomes smaller.

In the case of TF, there is a similar behavior than that observed for BAF_T . More precisely, for lower As concentrations in root, the As is distributed in the same proportion for the aerial parts of the plant, for instance, the As contained in leaf in ear is around 75% of the total As. However, for higher As concentration in root, TF suggest that the higher amount of

As is retained by root than by the aerial parts. Finally, a lower variation of BAF_T is observed for the CA than that found for CB. This behavior is related to the time of exposition of the root with higher As concentrations. This is, as time passes, the root stores higher amounts of As and thus accumulate higher As concentrations in the terrestrial structure.

In a related work, Rosas-Castor et al. (2014) sampled a region near to places with mineral activity in San Luis Potosi, Mexico. The authors found that one of the croplands irrigated with As concentrations around 23.6 mg L^{-1} presented a BAF_T lower than 0.14 for all the sampled points, whereas BAF_{TWE} ranges from 1.79 to 8.25. It is interesting to note that although the bioaccumulation factors found in the present

Table 6 Bioaccumulation and translocation factors

	As concentration ($\mu\text{g kg}^{-1}$)			BAF _T	BAF _{TWE}	TF
	Roots	Leaf	Ear			
CA						
M1	969	900.62		0.52	19.38	92.94
M2	991.83	989.33	< 24	0.50	19.84	99.75
M3	1290.32	987.29	< 24	0.57	25.81	76.52
CB						
M1	6210.38	1393.67		0.82	3.43	22.44
M2	18,196.33	1452.04	59.83	0.92	10.05	8.31
M3	21,940.16	4064.64	978.1	0.81	12.12	22.98

work are greater than that mentioned above, the difference might be related to the time that the contaminated irrigation water is used. Namely, in the present work, it is known that the contaminated water has been used for 30 years in the irrigation, suggesting that the time of exposure plays a central role in the bioaccumulation factors.

Effect of As in human health

In a previous research, near to the studied area in this work, it was found that the As in water is highly probable to be associated with some minerals contained in rocks. These results indicate that the As origin is mainly geogenic (Morales-Arredondo et al. 2016). However, the mining activities in these zones may cause As mobilization (Rosas-Castor et al. 2014). Areas of high As concentration in irrigation water show high As bio-accumulation in plant, livestock meat, milk, and cheese. Such elevated As concentrations in food may result in widespread health risk to the local and regional inhabitants (Bundschuh et al. 2012). These activities are mainly related to the inadequate use of well water for irrigation and animal water intake (Keshavarzi et al. 2011; Brahman et al. 2014; Sharifi et al. 2014). For barley, which is an important cereal crop in central Mexico, the brewing industry and its distilled seed remnants are used to feed ruminants, specifically, bovines which represent a potential threat to human health. As intoxication of ruminants is not common, since they are capable of tolerating concentrations close to $0.5 \mu\text{g L}^{-1}$. However, important amounts of As can be bioaccumulated in its organs and tissues (Zubair and Martyniuk 2018).

For most of the mammals including humans, the As entering the digestive system is rapidly adsorbed by the gastrointestinal tract and thus it is transported by the circulatory system to organs and tissues (Abdul et al. 2015). In many regions of the world, the consumption of different grains as cereals and legumes are part of the staple food, so their As concentration could be substantial contributors for total As exposure. For example, in Bangladesh, the rice exceeds the limits recommended by the WHO and represents the highest As source (Islam et al. 2017), while in Brazil, rice and beans are the main Brazilian staple food, with contributions ranging from 67 to 90% of the total As intake from food (Ciminelli et al. 2017). In the present work, the As concentration in the grain of barley (0.987 mg kg^{-1}) for CB exceeds the permissible levels established at $0.2 \text{ mg As kg}^{-1}$ by the FAO/WHO (2014). Furthermore, it has been shown that the concentration of As in soil and water is increasing over time; this increase of As in soil could increase the As in grain and might cause a higher concentration than the allowed levels established by the FAO/WHO (2014) even for irrigation water with low As concentrations ($< 25 \mu\text{g L}^{-1}$). Thus, a proper management of water in the croplands is an issue that needs to be addressed.

Conclusions

The presence of high levels of As (greater than $25 \mu\text{g L}^{-1}$) in irrigation water has increased the interest in understanding the mobilization mechanisms through the trophic chain as well as its potential damage in human health in the Bajío region. Moreover, the bioaccumulation of As in soil presents an additional concern that deserves a detailed investigation. The present work proceeds a step ahead, by providing a correlation through the bioaccumulation of As in the soil-plant system, As uptake, and a correlation between As and temperature in ground water.

The selected geostatistical model allows a fair representation of As concentration and temperature variabilities. High and low As concentration areas were remarkable in the spatial maps. The spatial distribution of high and low As concentration levels along the time is the same, which means highest As concentration areas remain in the same groundwaters. Also, average As concentration in groundwater increased from July 2009 to May 2010. Moreover, the spatial distribution maps of groundwater temperature show that the groundwaters with the highest temperature also presented the highest As concentrations. Even more, the geostatistical analysis indicates that As concentrations follow a leptokurtic distribution whereas the temperature follows a platykurtic distribution, implying a low dispersion of the As concentrations compared to the dispersion of the water temperature, suggesting a smoother changes in space of As concentrations than the ground water temperature. The As concentration variation over time shows a positive correlation suggesting that the As found in the first sampling date is related to the As concentration found at later dates. Besides, the higher the temperature in water, the higher the content of As. This relation suggests that as the temperature becomes higher, the As contained in the mineral rocks is mobilized as an effect of the temperature. That is, as the temperature is increased, the As is dissolved more easily in water favoring its mobilization. The temperature shows moderate quadratic correlations with As concentrations in water wells. However, further research is needed to understand better the relationship of As concentration and temperature in groundwater wells and the challenges they may represent for environmental care.

The As accumulated in plant parts always follow the order, As concentration in root > leaf > grain. Concentrations in grain could be increased. The results related to the BAF as well as the TF suggest the existence of a threshold which avoids the diffusion of the As into the aerial parts of the plant due to the high concentrations of As contained in the irrigation water (above 170 to $250 \mu\text{g L}^{-1}$). However, for concentrations in irrigation water around $25 \mu\text{g L}^{-1}$, the As in plant is distributed in the same proportion in the aerial parts of the plant in comparison with the terrestrial part. Since the As concentration found in grain for the CB exceeds the permissible limits in

grain for As concentration established by the FAO/WHO, it is important to establish a proper management of water in the croplands to alleviate this issue.

As a future work, it is interesting to investigate whether the high accumulation of As in soil is correlated to high availability of phosphorous in water and its relationship with As concentration in plant. The same phenomena are presented in plant. That is, a higher As concentration in soil and water is related to a high As accumulation in the barley structures.

Author's contributions Saldaña-Robles N. is an expert in geostatistical analysis and worked in the kriging and data analysis. Damián-Ascencio C. worked on the statistical correlations on the manuscript. Gutiérrez-Chávez contributed to the present work through the discussions regarding the impact of arsenic in the food chain. Zanor A.G. contributed to work through the characterization of soils and the discussion regarding the rocks and geological data. Guerra-Sánchez R. and Herrera-Díaz I. contributed to the chemical analysis and characterized the water and soil. Saldaña-Robles A. contributed to the work through the calculation and discussion of bioaccumulation and translocation factors as well as all the sampling of soil and water. Finally, all the authors contributed to the final version of the manuscript as well as its revision.

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Data Availability Not applicable.

Compliance with ethical standards

Ethics approval and consent to participate The authors approved and gave their consent to participate in the publication of the present work.

Consent for publication All the authors gave their consent for the publication of the present work.

References

- Abdul KSM, Jayasinghe SS, Chandana EP, Jayasumana C, De Silva PMC (2015) Arsenic and human health effects: a review. *Environ Toxicol Pharmacol* 40:828–846. <https://doi.org/10.1016/j.etap.2015.09.016>
- Batista BL, Souza JM, De Souza SS, Barbosa F Jr (2011) Speciation of arsenic in rice and estimation of daily intake of different arsenic species by Brazilians through rice consumption. *J Hazard Mater* 191:342–348. <https://doi.org/10.1016/j.jhazmat.2011.04.087>
- Bouyoucos GJ (1962) Hydrometer method improved for making particle size analysis of soils. *Agron J* 54:464–465. <https://doi.org/10.2134/agronj1962.00021962005400050028x>
- Brahman KD, Kazi TG, Baig JA, Afridi HI, Khan A, Arain SS, Arain MB (2014) Fluoride and arsenic exposure through water and grain crops in Nagarparkar, Pakistan. *Chemosphere* 100:182–189. <https://doi.org/10.1016/j.chemosphere.2013.11.035>
- Bundschuh J, Nath B, Bhattacharya P, Liu CW, Armienta MA, López-Moreno VM, López DL, Jean JS, Cornejo L, Lauer-Macedo LF, Tenuta-Filho A (2012) Arsenic in the human food chain: the Latin American perspective. *Sci Total Environ* 429:92–106. <https://doi.org/10.1016/j.scitotenv.2011.09.069>
- Carey AM, Lombi E, Donner E, De Jonge MD, Punshon T, Jackson BP, Guerinot ML, Price AH, Meharg AA (2012) A review of recent developments in the speciation and location of arsenic and selenium in rice grain. *Anal Bioanal Chem* 402:3275–3286. <https://doi.org/10.1007/s00216-011-5579-x>
- Carracelas G, Hombuckle J, Verger M, Huertas R, Riccetto S, Campos F, Roel A (2019) Irrigation management and variety effects on rice grain arsenic levels in Uruguay. *J Agric Food Res* 1:100008–100019. <https://doi.org/10.1016/j.jafr.2019.100008>
- Castor JMR, Portugal L, Ferrer L, Hinojosa-Reyes L, Guzmán-Mar JL, Hernández-Ramírez A, Cerdà V (2016) An evaluation of the bioaccessibility of arsenic in corn and rice samples based on cloud point extraction and hydride generation coupled to atomic fluorescence spectrometry. *Food Chem* 204:475–482. <https://doi.org/10.1016/j.foodchem.2016.02.149>
- Choudhury B, Chowdhury S, Biswas AK (2011) Regulation of growth and metabolism in rice (*Oryza sativa* L.) by arsenic and its possible reversal by phosphate. *J Plant Interact* 6:15–24. <https://doi.org/10.1080/17429140903487552>
- Ciminelli VS, Gasparon M, Ng JC, Silva GC, Caldeira CL (2017) Dietary arsenic exposure in Brazil: the contribution of rice and beans. *Chemosphere* 168:996–1003. <https://doi.org/10.1016/j.chemosphere.2016.10.111>
- D.O.F (1993) Norma Oficial Mexicana NOM-014-SSA1-1993. Diario Oficial de la Federación (D.O.F.). 16 de Diciembre de 1999
- D.O.F (1994) Norma Oficial Mexicana NOM-127-SSA1-1994. Diario Oficial de la Federación (D.O.F.). 17th October 2000
- Dahal BM, Fuerhacker M, Mentler A, Karki KB, Shrestha RR, Blum WEH (2008) Arsenic contamination of soils and agricultural plants through irrigation water in Nepal. *Environ Pollut* 155:157–163. <https://doi.org/10.1016/j.envpol.2007.10.024>
- Daya AA, Bejari H (2015) A comparative study between simple kriging and ordinary kriging for estimating and modeling the Cu concentration in Chehlkureh deposit, SE Iran. *Arab J Geosci* 8:6003–6020. <https://doi.org/10.1007/s12517-014-1618-1>
- FAO/WHO (2011a) Evaluation of certain contaminants in food. Seventy-second report of the Joint FAO/WHO Expert Committee on Food Additives. World Health Organization (WHO Technical Report Series, No. 959). Geneva
- FAO/WHO (2011b) Safety evaluation of certain contaminants in food. World Health Organization; Rome, Food and Agriculture Organization of the United Nations (WHO Food Additives Series, No. 63; FAO JECFA Monographs 8). Geneva
- FAO/WHO (2014) Expert Committee on Food Additives. Joint FAO/WHO Food Standards Programme Codex. Alimentarius Commission 37th Session: Report of the Eighth Session of the Codex Committee on Contaminants in Foods. Geneva
- Farooq MA, Islam F, Ali B, Najeeb U, Mao B, Gill RA, Yan G, Siddique KHM, Zhou W (2016) Arsenic toxicity in plants: cellular and molecular mechanisms of its transport and metabolism. *Environ Exp Bot* 132:42–52. <https://doi.org/10.1016/j.envexpbot.2016.08.004>
- Gustave W, Yuan ZF, Sekar R, Ren YX, Liu JY, Zhang J, Chen Z (2017) Soil organic matter amount determines the behavior of iron and arsenic in paddy soil with microbial fuel cells. *Chemosphere* 237:124459–124468. <https://doi.org/10.1016/j.chemosphere.2019.124459>
- Hossain FHJ, Bagtzoglou AC (2007) Geostatistically based management of arsenic contaminated ground water in shallow wells of Bangladesh. *Water Resour Manag* 21:1245–1261. <https://doi.org/10.1007/s11269-006-9079-2>
- Islam S, Rahman MM, Islam MR, Naidu R (2017) Geographical variation and age-related dietary exposure to arsenic in rice from Bangladesh. *Sci Total Environ* 601:122–131. <https://doi.org/10.1016/j.scitotenv.2017.05.184>

- Keshavarzi B, Moore F, Mosaferi M, Rahmani F (2011) The source of natural arsenic contamination in groundwater, west of Iran. *Water Qual Expo Health* 3:135–147. <https://doi.org/10.1007/s12403-011-0051-x>
- Lemos-Batista B, Nigar M, Mestrot A, Alves-Rocha B, Barbosa-Junior F, Price AH, Raab A, Feldmann J (2014) Identification and quantification of phytochelatin in roots of rice to long-term exposure: evidence of individual role on arsenic accumulation and translocation. *J Exp Bot* 65:1467–1479. <https://doi.org/10.1093/jxb/eru018>
- Li J, Heap A (2014) Spatial interpolation methods applied in the environmental sciences: A review. *Environ Model Softw* 53:173–189. <https://doi.org/10.1016/j.envsoft.2013.12.008>
- Lombi E, Scheckel KG, Pallon J, Carey AM, Zhu YG, Meharg AA (2009) Speciation and distribution of arsenic and localization of nutrients in rice grains. *New Phytol* 184:193–201. <https://doi.org/10.1111/j.1469-8137.2009.02912.x>
- Marques AP, Moreira H, Rangel AO, Castro PM (2009) Arsenic, lead and nickel accumulation in *Rubus ulmifolius* growing in contaminated soil in Portugal. *J Hazard Mater* 165:174–179. <https://doi.org/10.1016/j.jhazmat.2008.09.102>
- Mayorga P, Moyano A, Anawar HM, Garcia-Sanchez A (2013) Uptake and accumulation of arsenic in different organs of carrot irrigated with As-rich water. *CLEAN Soil Air Water* 41:587–592. <https://doi.org/10.1002/clen.201100697>
- Meharg A, Jardine L (2003) Arsenite transport into paddy rice (*Oryza sativa*) roots. *New Phytol* 157:39–44. <https://doi.org/10.1046/j.1469-8137.2003.00655.x>
- Meharg AA, Sun G, Williams PN, Adomako E, Deacon C, Zhu YG, Feldmann J, Raab A (2008) Inorganic arsenic levels in baby rice are of concern. *Environ Pollut* 152:746–749. <https://doi.org/10.1016/j.envpol.2008.01.043>
- Morales I, Villanueva-Estrada RE, Rodríguez R, Armienta MA (2015) Geological, hydrological, and geothermal factors associated to the origin of arsenic, fluoride, and groundwater, temperature in a volcanic environment BEI Bajío Guanajuatense, Mexico. *Environ Earth Sci* 74:5403–5415. <https://doi.org/10.1007/s12665-015-4554-9>
- Morales-Arredondo I, Rodríguez R, Armienta MA, Villanueva-Estrada RE (2016) The origin of groundwater arsenic and fluorine in a volcanic sedimentary basin in central Mexico: a hydrochemistry hypothesis. *Hydrogeol J* 24:1029–1044. <https://doi.org/10.1007/s10040-015-1357-8>
- Moreno-Jiménez E, Fernández JM, Puschenreiter M, Williams PN, Plaza C (2016) Availability and transfer to grain of As, Cd, Cu, Ni, Pb and Zn in a barley agri-system: Impact of biochar, organic and mineral fertilizers. *Agric Ecosyst Environ* 219:171–178. <https://doi.org/10.1016/j.agee.2015.12.001>
- Nieto-Samaniego AF, Ojeda-García AC, Alaniz-Álvarez SA, Xu S (2012) Geología de la región de Salamanca, Guanajuato, México. *Bol Soc Geol Mex* 64:411–425 ISSN 1405-3322
- Núñez O, Fernández-Navarro P, Martín-Méndez I, Bel-Lan A, Locutura JF, López-Abente G (2016) Arsenic and chromium topsoil levels and cancer mortality in Spain. *Environ Sci Pollut Res* 23:17664–17675. <https://doi.org/10.1007/s11356-016-6806-y>
- Ortega-Guerrero MA (2009) Occurrence, distribution, hydrochemistry and origin of arsenic, fluoride and other trace elements dissolved in groundwater at basin scale in central Mexico. *Rev Mex Cienc Geol* 26:143–161 ISSN: 1026-8774. WOS:000265165100011
- Praveen A, Mehrotra S, Singh N (2017) Rice planted along with accumulators in arsenic amended plots reduced arsenic uptake in grains and shoots. *Chemosphere* 184:1327–1333. <https://doi.org/10.1016/j.chemosphere.2017.06.107>
- Punshon T, Jackson BP, Meharg AA, Warczack T, Scheckel K, Guerinet ML (2017) Understanding arsenic dynamics in agronomic systems to predict and prevent uptake by crop plants. *Sci Total Environ* 581:209–220. <https://doi.org/10.1016/j.scitotenv.2016.12.111>
- Raab A, Wright SH, Jaspars M, Meharg AA, Feldmann J (2007) Pentavalent arsenic can bind to biomolecules. *Angew Chem Int Ed Engl* 119:2594–2597. <https://doi.org/10.1002/ange.200604805>
- Rahman MA, Hasegawa H, Rahman MM, Rahman MA, Miah MAM (2007) Accumulation of arsenic in tissues of rice plant (*Oryza sativa* L.) and its distribution in fractions of rice grain. *Chemosphere* 69:942–948. <https://doi.org/10.1016/j.chemosphere.2007.05.044>
- Rosas-Castor JM, Guzmán-Mar JL, Alfaro-Barbosa JM, Hernández-Ramírez A, Pérez-Maldonado IN, Caballero-Quintero A, Hinojosa-Reyes L (2014) Evaluation of the transfer of soil arsenic to maize crops in suburban areas of San Luis Potosi, Mexico. *Sci Total Environ* 497:153–162. <https://doi.org/10.1016/j.scitotenv.2014.07.072>
- Rothwell JJ, Taylor KG, Ander EL, Evans MG, Daniels SM, Allott TEH (2009) Arsenic retention and release in ombrotrophic peatlands. *Sci Total Environ* 407:1405–1417. <https://doi.org/10.1016/j.scitotenv.2008.10.015>
- Roychowdhury T, Tokunaga H, Uchino T, Ando M (2005) Effect of arsenic-contaminated irrigation water on agricultural land soil and plants in West Bengal, India. *Chemosphere* 58:799–810. <https://doi.org/10.1016/j.chemosphere.2004.08.098>
- Ruiz-Huerta EA, de la Garza Varela A, Gómez-Bernal JM, 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>
- Sabet-Aghlidi P, Cheraghi M, Lorestani B, Sobhan-Ardakani S, Merrikhpour H (2018) Spatial distribution of arsenic under the influence of chemical fertilizers using geostatistics in Eghlid, Fars, Iran. *Arch Hyg Sci* 7:303–311. <https://doi.org/10.29252/ArchHygSci.7.4.303>
- Sadee BA, Foulkes ME, Hill SJ (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.foodchem.2016.04.066>
- Saldaña-Robles A, Abraham-Juárez MR, Saldaña-Robles AL, Saldaña-Robles N, Ozuna C, Gutiérrez-Chávez AJ (2018a) The negative effect of arsenic in agriculture: irrigation water, soil and crops, state of the art. *Appl Ecol Environ Res* 16:1533–1551
- Saldaña-Robles A, Saldaña-Robles N, Saldaña-Robles AL, Ana-Zanor G, Ruiz-Aguilar GM, Gutiérrez-Vaca C (2018b) Phosphorus effect on arsenic accumulation of barley (*Hordeum vulgare* L.) through irrigation with contaminated water. *Agrociencia* 52:407–418 ISSN 2521-9766
- Secretaría de Economía (2016) Norma Mexicana NMX-AA-132-SCFI-2016. Diario Oficial de la Federación (DOF), 06 th March 2017
- Segura FR, de Oliveira-Souza JM, De Paula ES, da Cunha-Martins A Jr, Paulelli ACC, Barbosa F Jr, Batista BL (2016) Arsenic speciation in Brazilian rice grains organically and traditionally cultivated: is there any difference in arsenic content? *Food Res Int* 89:169–176. <https://doi.org/10.1016/j.foodres.2016.07.011>
- SEMARNAT (2000) Norma Oficial Mexicana NOM-021-SEMARNAT-2000. Diario Oficial de la Federación (DOF), 17 de Octubre de 2000
- Sharifi R, Moore F, Keshavarzi B (2014) Potential health risks of arsenic, antimony and mercury in the Takab geothermal field, NW Iran. *Int J Environ Stud* 71:372–390. <https://doi.org/10.1080/00207233.2014.919734>
- Sharma I (2012) Arsenic induced oxidative stress in plants. *Biologia* 67:447–453. <https://doi.org/10.2478/s11756-012-0024-y>
- Sharma S, Kumar R, Sahoo PK, Mittal S (2020) Geochemical relationship and translocation mechanism of arsenic in rice plants: a case study from health prone south west Punjab, India. *Groundw Sustain Dev* 10:10033–10043. <https://doi.org/10.1016/j.gsd.2020.100333>
- Shieh SS, Chu JZ, Jang SS (2005) An interactive sampling strategy based on information analysis and ordinary kriging for locating hot spot

- regions. *Math Geol* 37:29–48. <https://doi.org/10.1007/s11004-005-8746-9>
- Sommella A, Deacon C, Norton G, Pigna M, Violante A, Meharg AA (2013) Total arsenic, inorganic arsenic, and other elements concentrations in Italian rice grain varies with origin and type. *Environ Pollut* 181:38–43. <https://doi.org/10.1016/j.envpol.2013.05.045>
- Suriyagoda LD, Dittert K, Lambers H (2018) Mechanism of arsenic uptake, translocation and plant resistance to accumulate arsenic in rice grains. *Agric Ecosyst Environ* 253:23–37. <https://doi.org/10.1016/j.agee.2017.10.017>
- U.S. EPA (2000) Method 6010C (SW-846): inductively coupled plasma-atomic emission spectrometry, Revision 3. Washington, DC
- U.S. EPA (2007) Method 3051A (SW-846): microwave assisted acid digestion of sediments, sludges, and oils, Revision 1. Washington, DC
- Vamerali T, Bandiera M, Coletto L, Zanetti F, Dickinson NM, Mosca G (2009) Phytoremediation trials on metal-and arsenic-contaminated pyrite wastes (Torviscosa, Italy). *Environ Pollut* 157:887–894. <https://doi.org/10.1016/j.envpol.2008.11.003>
- Vercoutere K, Fortunati U, Muntau H, Griepink B, Maier EA (1995) The certified reference materials CRM 142 R light sandy soil, CRM 143 R sewage sludge amended soil and CRM 145 R sewage sludge for quality control in monitoring environmental and soil pollution. *Fresenius J Anal Chem* 352:197–202. <https://doi.org/10.1007/BF00322326>
- WHO (1981) Arsenic Environmental Health Criteria, No. 18. Geneva
- WHO (2008) Guidelines for drinking water quality, 3rd edn. World Health Organization, Geneva ISBN: 978 92 4 154761 1
- Yamamoto JK (2005) Correcting the smoothing effect of ordinary kriging estimates. *Math Geol* 37:69–94. <https://doi.org/10.1007/s11004-005-8748-7>
- Zahid A, Hassan MQ, Ahmed KMU (2015) Simulation of flowpaths and travel time of groundwater through arsenic-contaminated zone in the multi-layered aquifer system of Bengal Basin. *Environ Earth Sci* 73: 979–991. <https://doi.org/10.1007/s12665-014-3447-7>
- Zanor GA, García MG, Venegas-Aguilera LE, Saldaña-Robles A, Saldaña-Robles N, Martínez-Jaime OA, Segoviano-Garfias JJN, Ramírez-Santoyo LF (2019) Sources and distribution of arsenic in agricultural soils of Central Mexico. *J Soils Sediments* 19:2795–2808. <https://doi.org/10.1007/s11368-019-02269-8>
- Zhao FJ, Ma JF, Meharg AA, McGrath SP (2009) Arsenic uptake and metabolism in plant. *New Phytol* 181:774–794. <https://doi.org/10.1111/j.1469-8137.2008.02716.x>
- Zubair M, Martyniuk CJ (2018) A review on hemato-biochemical, accumulation and patho-morphological responses of arsenic toxicity in ruminants. *Toxin Rev* 38:176–186. <https://doi.org/10.1080/15569543.2018.1442347>
- Zvobgo G, Sagonda T, Lwalaba JLW, Mapodzeke JM, Muhammad N, Chen G, Shamsi IH, Zhang G (2018) Transcriptomic comparison of two barley genotypes differing in arsenic tolerance exposed to arsenate and phosphate treatments. *Plant Physiol Biochem* 130:589–603. <https://doi.org/10.1016/j.plaphy.2018.08.006>
- Zvobgo G, Lwalaba JLW, Sagonda T, Mapodzeke JM, Muhammad N, Shamsi IH, Zhang GP (2019) Alleviation of arsenic toxicity by phosphate is associated with its regulation of detoxification, defense, and transport gene expression in barley. *J Integr Agric* 18:381–394. [https://doi.org/10.1016/S2095-3119\(18\)61955-0](https://doi.org/10.1016/S2095-3119(18)61955-0)

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