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Comparing the Uptake of Arsenic by Barley and Oats Growing in a Semiarid Area Irrigated with Either Groundwater or Treated Wastewater

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Abstract: Groundwater and domestic wastewater are often used in conjunction with surface water to irrigate crops in semiarid areas. A concern associated with this practice is the potential accumulation of arsenic (As) and heavy metals in soil and plants, especially in places where irrigation water contains geogenic As. Studies on arsenic uptake in cereal crops growing under dry and oxidizing conditions are scarce. A one-year field experiment was conducted to evaluate the uptake and translocation of As in barley and oats irrigated with either groundwater (GW) or treated domestic wastewater (TWW) in northern Mexico. The content of As, as well as toxic metals Cd and Pb, were determined in soil and 24 sets each of barley and oat plants. Metal(loid)s accumulated more in the roots and leaves, and less in the stems and grains. Barley grains contained 0.2 mg/kg of As under GW or TWW, whereas oat grains contained twice this amount. Bioconcentration (BCF) and translocation (TF) factors were < 1 for As and Cd in plants irrigated with both GW and TWW indicating that neither barley nor oats are As-accumulators, and their grain and leaves can be safely used for fodder. However, oats irrigated with TWW bioaccumulated Pb in leaves. Conscientious monitoring of As and associated metals in soil and crops irrigated with TWW and GW is recommended.

Keywords: arsenic; lead; Chihuahua; semiarid; bioaccumulation; translocation factor

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1. Introduction

The availability of freshwater used for irrigation in arid and semi-arid regions is declining rapidly [1–3] and it is expected to be reduced even further due to global climate warming [3,4]. As a result, agricultural areas in arid and semi-arid areas often rely on wastewater and/or groundwater to satisfy their irrigation requirements [2,4–6]. This practice has many advantages and disadvantages, but if well managed (e.g., crops not consumed directly by humans) and properly monitored, it could contribute to food security and to the sustainability of water and soil resources [6,7].

The use of treated wastewater (TWW) for irrigation, besides providing much-needed water under arid and semi-arid conditions, practically eliminates the need for nitrogen fertilization, increases soil fertility, diminishes the risk of eutrophication, and saves energy [2]. However, TWW also contains salts, heavy metal(loid)s (HMs), emerging contaminants, and pathogens that may degrade the soil and crops [8–11]. Groundwater (GW) used for irrigation is also required to meet quality guidelines [12] with respect to e.g., salinity, as some Na salts are toxic to plants, in addition to toxic contaminants such as As, Se, and Cd, emergent contaminants, and pathogens. A particular concern is represented by staple foods contaminated with As due to the widespread contamination of As in groundwater worldwide [13], its toxic nature [14], and the relatively high mobility from soil to plant [15]. Other toxic metals generally studied in conjunction with As include cadmium (Cd) and lead (Pb). Oddly, studies on the uptake of As by barley and oats are very few, among them [16–19], despite these being common staple cereals. Barley growing in soil containing about 11 mg kg^{-1} of As had 0.10 mg kg^{-1} of As in leaves and 0.65 mg kg^{-1} of As in roots, while oats growing in the same soil had 0.27 mg kg^{-1} of As in leaves and 0.73 mg kg^{-1} of As in roots [16]. Reports on As uptake by wheat are relatively few as well, and report a small uptake of As compared to the uptake of other metals [4]. In contrast, there are multiple studies on the As content in rice growing in southeast Asia, since rice is a staple food and also a well-known As accumulator [20,21]. An information gap thus exists about the As uptake by crops other than rice that grow in semiarid areas such as the north of Mexico and the US Southwest, where the As sources, soil, and climatic conditions are quite different to those of Southeast Asia [22].

The toxicity of HMs to plants varies according to multiple factors, including concentration, the presence of other toxicants, climatic conditions, and the plant's own diverse physiological, biochemical, and molecular mechanisms against toxic substances [19,23,24]. As a result, the negative impacts to crop and soil irrigated with GW or TWW are highly variable depending on the type of contaminants present and their concentrations, irrigation frequency, climate, and soil and aquifer type [2,4,25]. Therefore, the response of crops and agricultural soil to the contaminants in irrigation water should be determined for each situation, often using field and greenhouse experiments [8,23,26,27].

Studies agree that bioaccumulation of metals and emergent contaminants in soils and crops may produce negative effects on human and ecosystem health, especially after long-term wastewater irrigation [1,9,28]. The expected health risks to humans are a function of the metal and the amount of metal bioaccumulation in crops. For example, Cao et al. [29] tested twenty crops and six HMs using pot experiments and identified three crops and three toxicants that posed a higher health risk to the population.

Crops used for fodder, such as barley and oats, are a favored choice of crop growing in soil rich in HMs because they are not directly consumed by humans and their resistance to the presence of heavy metals [19,30]. In addition to their tolerance to toxic metals [19], these crops, as well as other cereals, respond favorably to wastewater irrigation compared to well water with an increase in seed yield and leaf chlorophyll [8,27].

Regulations and recommended guidelines for the safe use of wastewater in agriculture are reported by various agencies, including the FAO, WHO, and US EPA, in addition to those issued by individual countries. However, most of these lists generally include only a few HMs. Seventy such guidelines for agricultural purposes from around the world were compiled into a review by Shoushtarian and Negahban-Azar [25]. Notably, a set of recommended values for HMs in TWW used for irrigation in arid and semiarid areas of Texas vary according to short- or long-term irrigation [31]. The values reported for short-term (<20 years) irrigation coincide with the values reported by the FAO [32]. Recommended guidelines for HMs in cereal grains are 0.2 mg kg^{-1} of As, 0.1 mg kg^{-1} of Cd, and 0.02 mg kg^{-1} of Pb [12].

The objectives of this study were to: identify the extent to which As, Cd, and Pb incorporate into barley (*Hordeum vulgare* L.) and oats (*Avena sativa* L.) after irrigating with TWW or GW; determine the bioaccumulation and translocation of HMs for each crop; to make recommendations based on the potential accumulation of As, Cd, and Pb over long-term irrigation in this water-scarce region whose groundwater contains geogenic As.

2. Materials and Methods

2.1. Description of the Study Area

The study area is located in northern Mexico on an elevated (1.300 m.a.s.l.) plateau that receives an average of 2.98 cm annual precipitation. The agricultural area is fed by the Rio Chuvíscar, a small river crossing the city of Chihuahua (pop. 900,000) in a west–east direction, after which it flows east–northeast. A wastewater treatment plant discharges its effluent into this river and the combined flow supports agriculture downstream (Figure 1). The main crops grown in this area include oats, corn, pecans, and alfalfa. Previous studies reporting HMs content in soils of this area are scant, among them are [33] for agricultural soils and [34] for stream sediments. Metal concentrations reported in the former are 68 to 155 mg kg^{-1} of Pb and 1.6 to 4.9 mg kg^{-1} of Cd, [33]. Arsenic concentrations in sediments are 30 mg kg^{-1} of As and 20 mg kg^{-1} of As for river and dry arroyos, respectively [34].

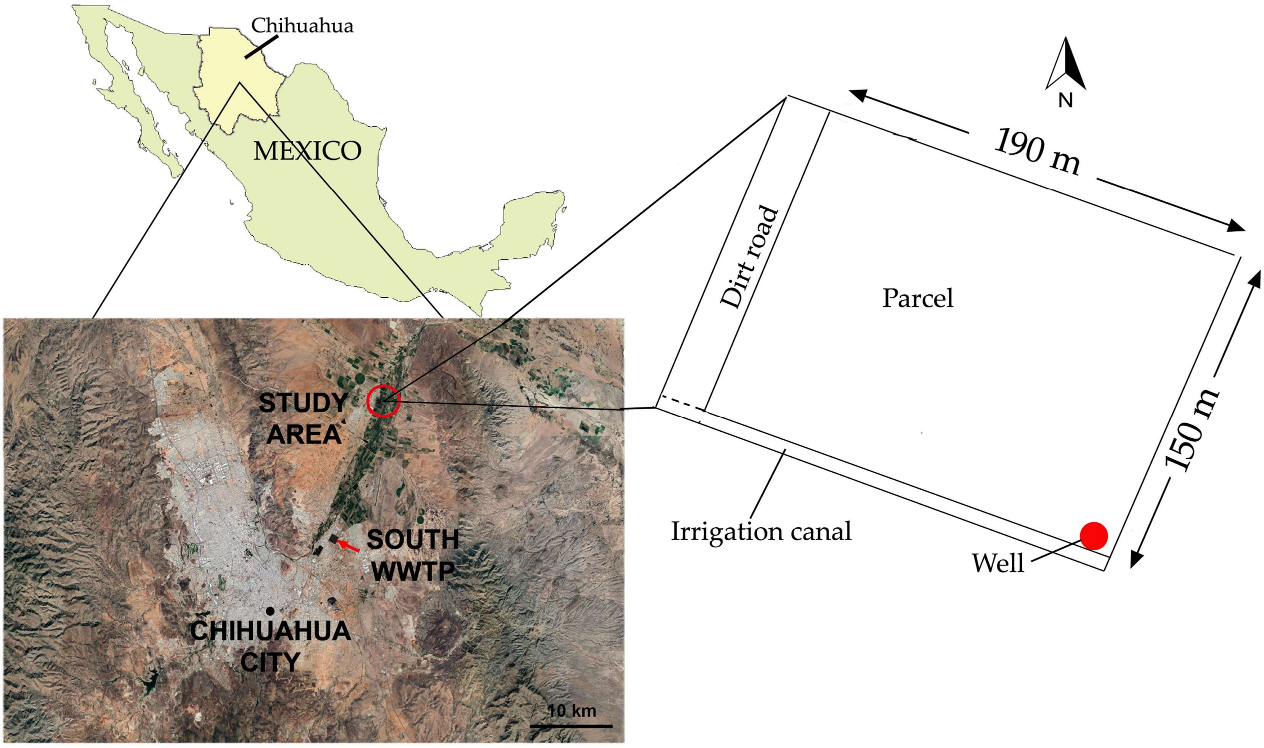

Figure 1. Location of the study area, showing the aridity of the surroundings and the strip of irrigated parcels downstream of the wastewater treatment plant.

Groundwater in the study region is drawn from several alluvial aquifers that interconnect in the subsurface, which contain naturally occurring As and fluoride (F) [35]. The aquifers underlying the study area are the Tabalaopa-Aldama and Aldama-San Diego, whose As concentration varies between the limit of detection (LOD) and 0.226 mg L^{-1}. The origin of As has been related to the weathering of volcanic rocks comprising the alluvium fill of the aquifers [35]. In a 2013 study conducted in this area, 18% of the well water samples surpassed the Mexican guideline of 0.025 mg L^{-1} of As and 51% surpassed the World Health Organization (WHO) guideline of 0.010 mg L^{-1} of As [35].

The temperature in the region starts at −5 °C during winter and may rise to 40 °C during the summer. The soil is calcisol, an alkaline soil that is typical of arid regions [36]. The field experiment was conducted on a rectangular agricultural parcel 190 m × 150 m centered at latitude 28°44′44.28″ N and longitude 105°57′28.52″ W. The soil preparation and cultivation are described in more detail in [37].

2.2. Groundwater and Treated Wastewater Utilized in Irrigation

Groundwater utilized in irrigation was drawn from a shallow (5 m deep) well, whose location is shown in Figure 1. About 45% of the wells in this area have a high content of naturally occurring As and fluoride (F^-) and 10% of wells have anthropogenic nitrate ($N\text{-}NO_3 > 10$ mg L^{-1}) in addition to the abovementioned natural contaminants [35].

The treated wastewater (TWW) used in this study was the effluent from the south wastewater treatment plant (WWTP) and has an average daily inflow of the WWTP is 1875 L s^{-1}. The WWTP treats domestic sewage using a secondary treatment and a final chlorine disinfection step. This plant has been in operation since 2006. Prior to 2006, untreated wastewater was discharged into the irrigation canal. The effluent of the WWTP is diverted to irrigate parcels (~800 L s^{-1}), provide gray water (~100 L s^{-1}), and the rest is discharged into the Chuvíscar River. The irrigation canal flows parallel to the Rio Chuvíscar (Figure 1).

2.3. Sample Collection

A total of 10 TWW and 10 GW samples were collected at regular intervals between planting and harvesting time. Water was sampled in clean 1-liter polyethylene bottles. Once collected, they were kept on ice at 4 °C until analysis upon arrival at the laboratory or within 24 h.

Soil samples were collected from three locations from the top 0.30 m depth and mixed to obtain one representative composite sample. Three replicates were used to check the reproducibility of the results. Once collected, soil samples were kept at 4 °C in a cooling box until they reached the laboratory where they were analyzed according to standard methodology (NOM-021-RECNAT-2000) [38].

2.4. Water Analyses

The pH, electrical conductivity (EC), temperature, and total dissolved solids (TDS) were estimated on-site with Pocket Pro+ Multi 2 Tester for pH/Cond/TDS/Salinity with Replaceable Sensor HACH® (HACH, Loveland, CO, USA). Samples were filtered using 0.45 µm membranes to determine the anion concentrations: Cl^-, NO_3, $SO_4{}^{-2}$, and $PO_4{}^{-3}$ by ion chromatography (DIONEX ICS-1100; Thermo Fisher Scientific, Waltham, MA, USA) following the US EPA Method 300 and an AS19 column (4 mm × 250 mm) and AERS 500 suppressor (4 mm). Quality assurance and quality control (QA/QC) included a certificated standard Dionex seven Anion Standard II (100 mL), blanks every 10 samples, and duplicates per sample. The linear correlation coefficient (r^2) for every anion was 0.995 or higher. The relative standard deviations (RSD) of the duplicates were <20%, indicating acceptable levels of accuracy.

The concentrations of HMs in TWW and GW were determined at the Mexican Geological Service (SGM) Laboratory in Chihuahua. The HMs were analyzed by atomic absorption spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, Model ELAN 6100®) according to the NMX-AA-131/1-SCFI-2019 method [39]. For QA/QC, blanks and duplicates were included.

2.5. Soil Characterization

The pH, electrical conductivity (EC), texture, cation exchange capacity (CEC), organic matter (OM), nitrate ($N\text{-}NO_3$), sodium adsorption ratio (SAR), exchange sodium percentage (ESP), and micro and macro nutrients determinations were carried out at the INIFAP Laboratory in Gomez Palacio. Available phosphorous was determined by the Olsen method, micronutrients (Fe, Mn, Zn, and Cu) were extracted by DTPA (diethylenetriaminepentaacetic acid). Exchangeable bases (Ca, Mg, K, and Na) in the soil were obtained using the ammonium acetate (1 N NH_4OAc at pH 7.0) extraction. HMs analyses were performed by mass spectrometry (ICP-MS, Perkin Elmer, Model ELAN 6100®) following the standard method [39] and conducted by the Servicio Geologico Mexicano's Laboratory in Chihuahua. The quality assurance and quality control (QA/QC) procedures included acid-washed glassware, reagent-grade chemicals, blanks every 10 samples, and duplicates per sample. All analyses followed Mexican Guidelines NOM-021-RECNAT-2000 and NMX-AA-131/1-SCFI-2019 [38,39].

2.6. Plant Analyses

The As, Cd, and Pb contents in plant tissue were determined as follows: 0.5 g of dried samples were digested in 5 mL of a mixture of nitric acid and perchloric acid 2:1 v/v. The mixture was heated at 120 °C for 45–60 min until the solution became clear. The temperature was increased to 240 °C until the sample was almost dry and then cooled down to room temperature. This digested sample was re-suspended with double-distilled water to reach a volume of 10 mL, centrifuged, and the solution was then used to determine its HMs after adding ammonium phosphate in an atomic absorption spectrometer with graphite furnace AAnalyst700 model Perkin Elmer. Cd and Pb required the addition of a modified matrix, and As required a palladium–magnesium modifier according to US EPA Methods 213-2, 239-2 y 206-2 [40], respectively. For QA/QC, blanks and duplicates per sample were included. These analyses were performed at the INIFAP laboratory in Gomez Palacio.

2.7. Bioconcentration and Translocation Factors

The nodes of cereal plants control the distribution of toxic metals to leaves and grains [14]. Bioconcentration factor (BCF), translocation factor for grain (TF_{grain}), and translocation factor for leaves (TF_{leaf}) were calculated according to Equations (1)–(3):

$$BSF = C_{edible\ part}/C_{soil} \tag{1}$$

$$TF_{grain} = C_{grain}/C_{root} \tag{2}$$

$$TF_{leaf} = C_{leaf}/C_{root} \tag{3}$$

If BCF > 1, the plant is considered an accumulator and if TF > 1 a translocator. For BCF and TF <1, the species can be considered a candidate for phytostabilization [10,29,41] (Cristaldi et al., 2020; Cao et al., 2022; Dovlatabadi et al., 2022).

2.8. Statistical Analysis

GW and TWW were compared using an unpaired t-test (Levene test), using F distribution, right-tailed [42] due to the small number of data (N = 10), and assuming a non-normal distribution of data. An online calculator www.statskingdom.com was utilized for this purpose. For water quality, TDS and As data were compared between GW and TWW. Similarly, the content of As in the root, grain, and leaves (N = 12) was also compared using this test to determine if the HM content of plants irrigated with GW and those irrigated with TWW were different. Standard deviation (SD) or standard error (SE) was calculated for each mean of water quality or HMs in plant parts, respectively.

3. Results

3.1. Water Quality

The results of the water quality parameters for GW and TWW are listed in Table 1 expressed as mean ± standard deviation and individual results in Table S1. Except for phosphorus, the inorganic parameters barely changed between GW and TWW. After applying the Levene test for equality of variances [42], the selected parameters As and TDS were no different (p > 0.05) between GW and TWW. The reason for the similar values can be explained as follows: groundwater supplying drinking water to the City of Chihuahua is treated (reverse osmosis) to remove As and other geogenic contaminants; however, the reverse osmosis waste is discharged back into the wastewater treatment plant, increasing the As concentration to roughly the original concentration, as observed in Table 1. Table 1 also shows that both GW and TWW are enriched in As, with an average of 0.037 mg L^{-1} and 0.051 mg L^{-1} of As, respectively. For comparison purposes, the average As groundwater concentration for the state of Chihuahua has been reported as 0.017 mg L^{-1} and the Mexican drinking water guideline for As is 0.025 mg L^{-1} although it is presently being lowered to 0.010 mg L^{-1} of As [43]. Irrigation water guidelines are listed in Table 2

Table 1. Water quality parameters of GW (N = 10) and TWW (N = 10). EC = electrical conductivity, TDS = total dissolved solids, TH = total hardness, SD = standard deviation, <LOD = below limit of detection.

Parameter	GW		TWW	
	Mean ± SD	Range	Mean ± SD	Range
pH	7.7 ± 0.5	7.2–8.9	7.8 ±0.5	7.3–8.8
EC, mS m^{-1}	1.0 ± 0.7	0.9–1.1	0.9 ±0.2	0.8–1.2
Temperature, °C	22.3 ± 4.6	17.1–31.1	21.5 ± 6.2	14.3–30.4
TDS, mg L^{-1}	681 ± 187	178–842	676 ± 108	570–848
TH, mg L^{-1} $CaCO_3$	359 ± 51	290–430	370 ± 51	300–440
Cl^-, mg L^{-1}	90 ± 27	60–161	70 ± 11	55–81
N-$NO_3{}^-$, mg L^{-1}	7.6 ± 2.8	<LOD–9.6	8.0 ± 3.0	3.0–13.7
$PO_4{}^{3-}$, mg L^{-1}	<LOD	<LOD	7.6 ± 0.9	6.3–8.8
$SO_4{}^{2-}$, mg L^{-1}	138 ± 20	96–168	109 ± 17	84–124
As, mg L^{-1}	0.037 ± 0.017	0.009–0.057	0.051 ± 0.013	0.037–0.069
Cd, mg L^{-1}	< LOD	<LOD	< LOD	<LOD
Pb, mg L^{-1}	< LOD	<LOD	< LOD	<LOD

Table 2. Guidelines for heavy metals in irrigation water.

	As, mg L^{-1}	Cd, mg L^{-1}	Pb, mg L^{-1}	Reference
FAO	–	0.01	5	Ayers and Westcot, 1994 [32]
Fipps – long-term irrigation	0.10	0.01	5	Fipps, 2003 [31]
Fipps – short-term irrigation	2.0	0.05	10	Fipps, 2003 [31]

3.2. Soil Characterization

The soil physicochemical parameters are shown in Table 3 and soil HM content in Table 4.

Table 3. Soil physicochemical characterization for each of the three soil samples (samples 1, 2, 3). SAR= Sodium adsorption ratio, ESP= Exchange sodium percentage.

Parameter	1	2	3	Parameter	1	2	3
pH	8.51	8.46	8.44	Extractable K, mg kg^{-1}	694	903	895
EC, dS m^{-1}	1.17	1.05	1.01	Extractable Ca, mg kg^{-1}	4102	4826	4702
Texture		clay loam		Extractable Mg, mg kg^{-1}	449	481	388
CEC, mg in 100 g	36.0	38.0	32.7	Extractable Fe, mg kg^{-1}	0.6	1.2	0.7
OM, %	1.30	1.50	1.50	Extractable Mn, mg kg^{-1}	2.66	2.30	2.30
N-NO_3, mg kg^{-1}	29.1	17.8	9.5	Zn, mg kg^{-1}	2.01	2.79	3.31
N-NH_4, mg kg^{-1}	14.9	13.3	6.5	SAR	4.24	4.65	5.34
Available P, mg kg^{-1}	8.2	10.8	12.8	ESP	5.89	7.30	6.48

Table 4. Metal(loid)s in soil (N = 1, one composite soil sample).

Metal(loid)	mg kg^{-1}	Metal(loid)	mg kg^{-1}	Metal(loid)	mg kg^{-1}
Ag	1	Cr	59	Pb	63
Al	115,100	Cu	11	Se	3
As	19	Fe	30,700	Sr	206
Ba	548	Mn	604	Tl	1
Be	4	Mo	2	V	59
Cd	1	Ni	13	Zn	116

3.3. Metal(loid) Uptake by Plants

HM uptake by barley and oats is listed in Table 5 as average ± standard error and individual results in Table S2. The HMs content in grain can be compared with the recommended limits for As, Cd, and Pb in grain of 0.02 mg kg^{-1}, 0.01 mg kg^{-1}, and 0.02 mg kg^{-1}, respectively [12].

Table 5. Average ± standard error of metal(loid)s in barley and oats irrigated with either groundwater (GW) or treated wastewater (TWW).

	GW (N = 12)			TWW (N = 12)		
	As	**Cd**	**Pb**	**As**	**Cd**	**Pb**
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Barley:						
Root	3.10 ± 0.32	0.648 ± 0.068	10.32 ± 1.42	2.54 ± 0.20	0.836 ± 0.108	9.85 ± 0.89
Stem	0.62 ± 0.12	0.142 ± 0.015	1.07 ± 0.40	0.43 ± 0.08	0.178 ± 0.012	0.18 ± 0.07
Leaves	2.27 ± 0.15	0.190 ± 0.025	2.27 ± 0.39	1.98 ± 0.17	0.256 ± 0.016	1.84 ± 0.19
Grain	0.20 ± 0.04	0.011 ± 0.003	0.13 ± 0.03	0.26 ± 0.05	0.020 ± 0.005	0.09 ± 0.06
Oats:						
Root	2.54 ± 0.60	0.360 ± 0.030	136.94 ± 33.20	2.30 ± 0.42	0.423 ± 0.016	88.71 ± 8.93
Stem	1.53 ± 0.50	0.100 ± 0.010	46.59 ± 2.42	0.54 ± 0.44	0.120 ± 0.008	45.07 ± 7.57
Leaves	1.19 ± 0.60	0.180 ± 0.020	125.42 ± 5.60	1.49 ± 0.21	0.209 ± 0.014	132.50 ± 14.10
Grain	0.55 ± 0.25	0.030 ± 0.010	49.96 ± 1.84	0.39 ± 0.28	0.015 ± 0.003	68.30 ± 11.40

4. Discussion

The soil of the studied area has been irrigated with TWW for several decades, a period long enough to allow the soil to stabilize with respect to solutes contained in TWW, including HMs, nutrients, and organic matter (Tables 3 and 4) and resulting in a soil containing 19 mg kg^{-1} of As. This is the first report of As content in soils in this region and fits within the reported 33.0 mg kg^{-1} of As in sediments of the nearest reservoir, 20.3 mg kg^{-1} of As in river sediment, and 10.2 mg kg^{-1} of As background value [34]. Irrigation water, either as TWW or GW, contained about the same concentration of As, about 0.045 mg L^{-1} of As, which surpassed the recommended guidelines of both Mexico (0.025 mg L^{-1}) and the WHO (10 mg L^{-1}). The uptake of As into barley and oats has not been previously reported for northern Mexico, despite this area ranking first in Mexico's oat production.

In plants, As accumulated primarily in the roots and least in grain in either barley or oats, as shown in Tables 5 and 6. The As content in each part of the plant (root, leaves, stem, and grain) was the same (according to Levene's test) between plants irrigated with GW and those irrigated with TWW. However, there was a significant difference ($p < 0.05$) in the As content between barley and oats for each of the grains, stems, and roots.

Although botanically similar, HMs accumulation in grains of barley or oats differed significantly; oats accumulated more As than barley despite the fact that the As in roots was about the same in either crop, in agreement with other studies [16]. The edible part of both plants is the grain, however, the leaves and stems may also be used as fodder for cattle. The grain of barley contained As values at or near the recommended guidelines (0.2 mg kg^{-1}) whereas leaves contained about 1.5 mg kg^{-1} of As. In oats, the amount of As in grains was about twice the amount in barley but the leaves accumulated slightly less As. The As content in barley grains fell within values reported for other world regions, 0.04 – 0.07 mg kg^{-1} [16,44].

The difference in metal uptake and translocation between barley and oats has been explained by their different mechanisms to deal with metal stress, either producing an increase (oats) or decrease (barley) in soluble sugars and protein in plant tissue [17,19,45]. The amount of metal assimilated by plants is reported to be a function of many factors, including temperature, soil mineralogical and bacteriological composition, HMs, and organic matter content [24]. For As, its speciation as either arsenite or arsenate has also been reported to affect accumulation, with arsenite uptake being several times greater than arsenate uptake (Su et al. 2010) [20]. The alkaline conditions of both soil and water in this study suggest that As occurs primarily as arsenate. The similar soil chemistry and temperature of the various samples collected within the study area (Table 3) indicate a relatively homogeneous soil. Therefore, the differences in metal accumulation are due to the inherent uptake and translocation mechanisms of either barley or oats and the solutes present in the irrigation water. Also, differences between GW and TWW were not statistically significant with respect to their content of TDS, As, and other solutes, except for phosphate, which was enriched in TWW (Table 1) and is relevant to this study as it aids in the accumulation and translocation of As [24]. However, the difference in phosphate was not large enough to have an effect on the accumulation of As in either barley or oats (Tables 5 and 6).

A measure of the bioaccumulation and translocation of metals in plants is compiled in Table 6. The bioaccumulation factor BCF < 1 obtained for As in barley indicates that this plant is tolerant to As and it is not an accumulator, as has been reported for other regions in Mexico [18,19] and elsewhere [16,20,44,45]. The results obtained here for barley growing in a soil containing 19 mg kg^{-1} of As also agree with the tolerance reported by a study using soil spiked with several concentrations of As [45], where the BCF and TF of barley growing in soils up to 50 mg kg^{-1} remained unchanged and an accumulation was first observed when the As content in soil was about 100 mg kg^{-1}.

BCF, TF_{grain}, and TF_{leaves} were all < 1 for As, Cd, and Pb in both crops, except for Pb in the root and leaves of oats, where values up to 2.17 for BCF were obtained (Table 6). However, leaves contain three-fold the amount of Pb compared to stems, for which combining leaves and stems for cattle feed would result in a smaller Pb content compared to that of leaves alone.

Table 6. Bioconcentration factor (BFC), translocation factor for grain (TF_{grain}), and translocation factor for leaf (TF_{leaf}) in barley and oats. N = 24 samples for each barley and oats; half of these were irrigated with GW and half with TWW.

	Irrigation source	Barley			Oats		
		As	Cd	Pb	As	Cd	Pb
BCF	GW	0.16	0.65	0.16	0.13	0.36	2.17
	TWW	0.13	0.84	0.16	0.12	0.42	1.41
TF_{grain}	GW	0.06	0.02	0.01	0.22	0.08	0.36
	TWW	0.08	0.02	0.01	0.15	0.03	0.77
TF_{leaf}	GW	0.73	0.29	0.22	0.47	0.50	0.92
	TWW	0.78	0.31	0.19	0.59	0.50	1.49

The tolerance of barley and oats to As has been documented by several studies [19,27,44], often comparing it to rice. The As uptake and translocation are reportedly facilitated by phosphate and silicon transporters [14,24], as well as by organic matter (OM). HMs translocate from the root to shoots through xylem vessels and are deposited in vacuoles where they remain removed from cytosol [23]. The increase in soil OM content may result in the reducing of conditions that favor the reduced form of As, arsenite, to be uptaken, as well as conditions that increase the mobility of As in soil and the bioavailability of As to plants [24]. However, these mechanisms are particular to As and do not necessarily apply to Cd and Pb. Cd accumulation is facilitated by Mn, Fe, and Zn transporters, whereas the mechanisms responsible for the uptake and translocation of Pb are not completely known [14,17].

Phytoremediation is one of the most recommended treatments to reduce metal content in soils. This is achieved using hyperaccumulator plants, several of which have been identified for each metal [23]. Growing crops that are tolerant to metals is a variation of this strategy [29] since plants can be altered genetically to diminish their metal uptake [14]. A suite of soil amendments can also increase the tolerance of plants to HMs and reduce the uptake, among them are thiol-rich compounds [14,24].

Barley and oats are tolerant to salinity and grow well in semiarid areas. Our results found a low As content in grains and a moderate As content in the leaves of both. Therefore, these crops offer a viable alternative to growing foodstuff while removing nutrients from TWW. The accumulation of As in soil was low to moderate (19 mg kg^{-1}) after decades of being irrigated with TWW and the As content in grain was low (0.02 to 0.04 mg kg^{-1}) at a level listed as safe by FAO [12]. Other metal content attenuation factors in plants and soil, respectively, are the non-linear increase in metals in crops with respect to metals in soil [1,4,46] and the periodic flushing of contaminants during the intense rain showers that typically occur in this region every five years or so [35]. Nevertheless, conscientious monitoring of HMs in soil and plants is recommended.

5. Conclusions

The results reported here fill an important gap in the knowledge on the uptake of As by two little-studied cereal crops, barley and oats, grown under alkaline soils in semiarid areas. The As uptake of barley and oats was low for the grain and moderate for leaves, suggesting that cultivation of these forage crops contributes to the sustainable management of water resources by removing nutrients from TWW and reducing the amount of GW extracted for irrigation. These processes contribute considerably to the conservation of water in this water-scarce area.

No significant difference in As content was found between TWW and GW nor between crops irrigated with TWW or GWW, despite TWW containing more phosphate (a known As transporter) than GW but there was a significant difference between barley and oats, with an increased As content in oats. Bioaccumulation and translocation factors were <1 for As in both crops, indicating that these plants are not accumulators of As. A spinoff result of this study was the finding that oat leaves accumulated lead, albeit slightly (BCF 1.4, TF_{leaf} 1.4). However, the TF for oat grains remained below 1.

Based on the above results, the cultivation of barley and/or oats is recommended as a safe and sustainable practice in this agricultural region whose groundwater contains high concentrations of geogenic As. Although neither barley nor oat accumulated As or Cd in any parts of the plant, barley plants outperformed oats based on their lesser uptake of As, Cd, and Pb. Close monitoring of the content of As and heavy metals in plants and soil is recommended. Studies determining other toxic solutes potentially present, such as emergent contaminants, are needed.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min13020175/s1, Table S1: Analysis of groundwater (GW) and treated wastewater (TWW) samples with replicates (a,b); Table S2: As, Cd, and Pb content in the root, grain, leaves, and stems (in mg kg^{-1} dry weight) of plants irrigated with groundwater (GW) or treated wastewater (TWW).

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