

## Research Article

# Arsenic III, V and total in canal irrigation water and transported load to rice fields of district Tando Muhammad Khan, Sindh-Pakistan

Muhammad Chohan<sup>1</sup>, Mehrunisa Memon<sup>1\*</sup>, Inayatullah Rajpar<sup>1</sup> and Muhammad Saleem Akhtar<sup>2</sup>

1. Department of Soil Science, Sindh Agriculture University, Tandojam, Sindh-Pakistan

2. PMAS Arid Agriculture University Rawalpindi-Pakistan

\*Corresponding author's email: [nisamemon@gmail.com](mailto:nisamemon@gmail.com)

### Citation

Muhammad Chohan, Mehrunisa Memon, Inayatullah Rajpar and Muhammad Saleem Akhtar. Arsenic III, V and total in canal irrigation water and transported load to rice fields of district Tando Muhammad Khan, Sindh-Pakistan. Pure and Applied Biology. Vol. 9, Issue 1, pp491-500. <http://dx.doi.org/10.19045/bspab.2020.90054>

Received: 24/10/2019

Revised: 30/11/2019

Accepted: 05/12/2019

Online First: 06/12/2019

### Abstract

Canal irrigation water coupled with city and industrial waste can increase the arsenic levels in sub-distributary canals and transfer arsenic into associated fields, rice grain and ultimately the human food chain. The trivalent arsenite  $[\text{AsO}_3]^{3-}$  and pentavalent arsenate  $[\text{AsO}_4]^{3-}$  (As-III and As-V) are the dominant and most toxic species in water. We investigated total and inorganic arsenic i.e. (As-III and As-V) in the irrigation water of District Tando Muhammad Khan, Sindh-Pakistan that was contaminated by different effluents and applied to rice fields. We also assessed total arsenic load transported to associated rice fields with the passage of time. Atomic Absorption Spectrometer equipped with Hydride Vapor Generation Assembly was employed to determine arsenic in water. The inorganic As-III fraction ( $4.21\text{-}51.47 \mu\text{g L}^{-1}$ ) was dominant over As-V ( $3.03\text{-}36.68 \mu\text{g L}^{-1}$ ). Three out of twenty four rice irrigation sites were above the prescribed limits of  $50 \mu\text{g L}^{-1}$  for irrigation by World Health Organization (WHO). High concentration of total arsenic ( $102.18 \mu\text{g L}^{-1}$ ) was due to arsenic coming from city ( $28.78 \mu\text{g L}^{-1}$ ), animal ( $26.76 \mu\text{g L}^{-1}$ ), cement factory, textile mills ( $31.42 \mu\text{g L}^{-1}$ ) and sugar industries ( $36.24 \mu\text{g L}^{-1}$ ) entering at Hyderabad and Tando Muhammad Khan. The water usage of  $1000\text{-}1300 \text{ mm a}^{-1}$  will transport  $0.065\text{-}0.085 \text{ mg kg}^{-1}$  of As-III,  $0.045\text{-}0.058 \text{ mg kg}^{-1}$  of As-V and  $0.12\text{-}0.16 \text{ mg kg}^{-1}$  of total arsenic per year in rice fields. Currently, these values are below the prescribed limit of  $50 \text{ mg kg}^{-1}$  for soils, however, can accumulate more in coming decades.

**Keywords:** Akram; As-III; As-V; Fuleli; Indus river

### Introduction

Arsenic is distributed all over the environment, originating from natural sources such as rocks, minerals and volcanoes. It enters the rivers, canals or sub-irrigation distributaries through disposal of arsenic contaminated waste along the way, eventually contaminating the agricultural lands. Inorganic forms of

arsenic i.e. trivalent arsenite  $[\text{AsO}_3]^{3-}$  and pentavalent arsenate  $[\text{AsO}_4]^{3-}$ , commonly referred as As-III and As-V, are more toxic than organic and gaseous forms due to their high degree of solubility. As a result, speciation of arsenic is of great significance. About 57-90% of the total arsenic in water is in inorganic form [1]. Compared to As-V, As-III, the reduced

form of arsenic is more mobile, toxic and therefore dominant under flooded soil environment. The oxidation-reduction, precipitation and adsorption processes in soil enhance the transport of both As-III and As-V from surface water into the soil environment.

Natural sources and anthropogenic activities discharge effluents into waterways, both sources transport arsenic to the environment through water. Irrigation water supplied in many countries, including Pakistan, contains significant quantities of dissolved arsenic and other heavy metals, as the municipal and industrial wastewater is directly discharged into open drains and nearby natural water bodies [2]. The main canals irrigating district Tando Muhammad Khan are Fuleli and Akram Wah, carrying water from the left bank of River Indus at Kotri Barrage. When these canals pass through Hyderabad city, highly toxic industrial waste (1.5 million gallons per day) and sewage water is directly dumped into these canals [3].

The trail of arsenic to human body is direct intake of As-contaminated drinking water or/and through the food chain [4]. Prolonged use of even low-arsenic contaminated water on agricultural lands could result in high soil arsenic accumulation [5]. The consumption of arsenic contaminated food products ultimately place human health at a high degree of risk. Local farmers of the study area generally grow rice under flooded conditions, which may carry larger quantities of arsenic in rice fields over those which are grown in upland environment. This, coupled with the eating habits of Asian people, where rice is the major part of their daily diet, makes it a matter of concern. Prolonged intake of arsenic contaminated rice can be the cause of cancer, cardiovascular diseases, inactivation of enzymes, growth inhibition and sudden death [6-8].

Research related to arsenic in surface and underground water is well documented in Pakistan [9-13]. Majority of these studies

provide information on total arsenic enrichment in water. However, there are very few studies on the speciation of inorganic arsenic [11], yet those pertaining to rice fields receiving arsenic contaminated canal irrigation water are completely missing. The main purpose of this study was to estimate As-III, As-V and total arsenic in canal irrigation water, each at the entrance of the associated rice field in Tando Muhammad Khan and appraise the amount of arsenic coming from city waste or industrial effluents in the vicinity of the study area. Based on the quantity of irrigation water and each arsenic form assessed in rice fields, the future arsenic load transported to associated rice soils was determined.

## Materials and methods

### Study area

District Tando Muhammad Khan (24°50' to 25°09' N and 68°19' to 68°32' E) is situated in south-east of Sindh province in Pakistan. The area is under semiarid, subtropical climate with less than 200 mm rainfall and temperature range of 8-47°C. Majority of the population is settled in villages and engaged in agriculture growing rice as a major food crop. The source of irrigation water for rice fields in the district is the sub-distributary canals i.e. Fuleli and Akram Wah originating from Indus River. The canal irrigation water is contaminated as it receives huge quantities of hazardous solid and liquid waste (sewage, sugar industry and city based waste) of Hyderabad city and Tando Muhammad Khan along the way (Fig. 1).

### Sampling

Total 24 rice fields were selected and canal irrigation water samples were collected at the entrance of each rice field. In each case, the sampling location was determined through global positioning system (GPS) using GPS-301 receptor meter. Samples were collected in plastic bottles rinsed with 10% nitric acid and deionized water. Six samples, 20-30 cm deep, at low flow conditions were collected from each site, composited and preserved by adding few

drops of phosphoric acid to avoid changes in oxidative state of arsenic. Prior to acidification, some physical and chemical parameters as pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature were recorded on the spot, using pH/EC/TDS/Temperature Meter (HI-9813-5, Hanna Instruments, USA). The samples were kept in ice box, transported on the same day to the laboratory, stored in dark and preserved at 4°C [13].

### Analytical methods

Total arsenic and arsenic speciation in canal irrigation water was determined by the method as outlined by Chappell *et al.* [14]. For extraction of arsenic, a 30 ml quantity of each sample was digested in 10M hydrochloric acid (HCl), shaken for 30 minutes (Lab-Line 3591, Melrose Park Ill) and filtered through 0.45µm filter paper. The filtrate was used for the determination of total arsenic.

For the determination of As-III, a 10 ml aliquot of the same extract, along with 80 ml of 10M HCl (Riedel-de-Haens) was placed in a 100 ml separatory funnel. In the next step, the contents were extracted for As-III using a 10 ml quantity of chloroform. This process of extraction was repeated four times and every time the aqueous acid phase was discarded. In order to back-extract As-III from organic phase, the contents in the separatory funnel were extracted with 20 ml of deionized water and the process was repeated and the contents were diluted to 100 ml volume and used for As-III determination. For total inorganic arsenic, 100 ml tubes containing 10 ml aliquot and 10 ml of 50% potassium iodide (KI) were placed on a water bath at 60°C for 25-30 minutes. The contents were cooled at room temperature and the volume was raised to 50 ml with distilled water. A 10 ml quantity of the solution was placed in a separatory funnel and the extraction of inorganic arsenic was carried out by using chloroform and deionized water. The process was repeated in the same way as in case of As-III.

All the extracts were separately used to determine total, total inorganic and As-III on Atomic Absorption Spectrometer (Shimadzu, Model No. AA-6300, Japan) equipped with Hydride Vapor Generation Assembly (Shimadzu, Model No. HVG-1, Japan). A hollow cathode lamp of arsenic was used as a radiation source at 193.7nm wavelength and spectral slit width of 0.7nm. The carrier solution for the hydride generation module was 10% HCl at a flow rate of 10 ml m<sup>-1</sup> and the reducing solutions were 0.5% sodium borohydride (NaBH<sub>4</sub> - Alfa Aesar) in 0.05% sodium hydroxide (NaOH - Riedel-de-Haens) at the flow rate of 5 ml m<sup>-1</sup>. The detection limit was 0.42 µg L<sup>-1</sup> calculated by analyzing 10 blanks, which had mean of 0.14 × the standard deviation (σ) 0.097. The concentration of As-V was calculated from the difference between total inorganic and As-III.

### Interpretation

The data for temperature, EC, pH, TDS, As-III, As-V and total arsenic were separately used to run descriptive statistics (range, mean and standard deviation). All the mentioned parameters were compared with the prescribed limits of irrigation water as given by FAO [15]. The mean arsenic concentration of 24.25 µg L<sup>-1</sup> in the irrigation water was used to calculate the total arsenic load transported from water to soil. The arsenic load was calculated separately for As-III, As-V and total arsenic from net (1000-1300 mm a<sup>-1</sup>) and gross (1700-2250 mm a<sup>-1</sup>) quantity of irrigation water applied to rice crop in Pakistan as reported by FAO [16].

## Results and discussion

### Physical and chemical parameters

The analytical data of 24 irrigation sites (Table 1) showed a temperature range from 31.10 to 32.71 °C, pH from 7.10 to 8.30, EC from 0.40 to 1.93 dS m<sup>-1</sup> and TDS from 220 to 960 mg L<sup>-1</sup>). Comparison of these data with permissible limits for irrigation water [17] showed that pH (7.10-8.30) was within the permissible range of 6.5-8.4, EC (0.40-1.93 dS m<sup>-1</sup>) of 66% (17) sites was below the permissible limit of 0.7 dS m<sup>-1</sup> having

no degree of restriction on irrigation. The EC of remaining 36% (07) sites was in the range of 0.7-3.00 dS m<sup>-1</sup> having slight to moderate effects. However, there were no sites having EC >3.0 dS m<sup>-1</sup>, which could have severe effects on soil or crop yields [17]. The TDS values (220-960 mg L<sup>-1</sup>) of 83% (20) sites were below the permissible limit of 450 mg L<sup>-1</sup> indicating no degree of restriction for irrigation. While, only 17% (4) sites were in the range of 450-2000 mg L<sup>-1</sup>, showing slight to moderate degree of restrictions on its use [17]. The EC and TDS contamination level of canal water bodies near by the study area (i.e. district Badin) was reported to be relatively much lower than that for groundwater [18]. The EC and pH of the water samples from Jamshoro and Khairpur districts of the same province were reported to be in the range of 0.40-3.72 dS m<sup>-1</sup> and 7.0-7.7, respectively [11,19].

#### Arsenic forms

As-III occurred as the dominant form (Fig. 2) (mean 13.06 µg L<sup>-1</sup>), representing 54% of total arsenic (mean 24.25 µg L<sup>-1</sup>), while As-V (mean 8.97 µg L<sup>-1</sup>) accounted 37% of the total arsenic present in water samples (Table 2). Together, As-III and As-V constituted 91% of the total inorganic arsenic, leaving 9% as residual (others) arsenic (0.05 to 14.03 µg L<sup>-1</sup>) (Fig. 3). Given the range of As-III as 4.21-51.47 µg L<sup>-1</sup>, there was only one sample which exceeded the permissible limit of 50 µg L<sup>-1</sup> [15]. However, there was no contamination observed with regard to As-V which ranged from 3.03-36.68 µg L<sup>-1</sup>. These values of As-III and As-V are much higher than those (As-III 3.08-4.35 As-V 2.32-3.85 µg L<sup>-1</sup>) reported by Baig *et al.* [11] for the canal water samples of Talukas Faiz Ganj, Thari Mirwah and Gambat of district Khairpur of Sindh province. This is particularly because the study area is located at the tail-end of river Indus, therefore, receives relatively a larger amount (1.5 million gallons per day) of industrial waste and sewage at Hyderabad [3]. Other studies such as those conducted in China [20] and Poland [21]

also report the dominance of As-III in surface water. This is reported to be basically due to industrial effluents [25], however, and it may vary due to large redox gradients as well as the seasonal variations in different regions such as in Pakistan [22]. A better picture can be presented based on the total arsenic (8.13-102.18 µg L<sup>-1</sup>) concentration showing that only 3 out of 24 canal irrigation sites associated with rice fields were above the prescribed limits of 50 µg L<sup>-1</sup>. These 3 sites having respective total arsenic concentration of 51.72, 57.23 and 102.18 µg L<sup>-1</sup> were in the surroundings of the city area and the water directly discharged from there into rice fields. Majority of the studies [10, 19] evaluating arsenic concentration are related to groundwater (including dug wells, tube wells and hand pumps), with a few focusing on surface water, which is a major source of irrigation used on agricultural lands in the country. Studies show that the total arsenic concentration is relatively higher (106 µg L<sup>-1</sup>) in ground water than in surface water of city, canal or municipal water as reported for Jamshoro (3-37 µg L<sup>-1</sup>, mean 15 µg L<sup>-1</sup>) and Khairpur (8.0 µg L<sup>-1</sup>) districts [11, 19]. However, total arsenic concentration obtained in this study was much lower than that reported for Manchar Lake (35.2-158 µg L<sup>-1</sup>, mean 97.5 µg L<sup>-1</sup>) [10] and water supply schemes of district Larkana [23]. The baseline arsenic concentration of river water originating from the Indus River to Fuleli (6.32 µg L<sup>-1</sup>) and Akram Wah (7.64 µg L<sup>-1</sup>) at Kotri Barrage was much lower compared to the arsenic concentration of industrial effluent and city waste of Hyderabad, Tando Muhammad Khan and the surroundings (Table 3). This confirms that the higher arsenic concentrations in sub-distributary canals entering associated rice fields are the result of anthropogenic activities and that the original river water of the Indus is not contaminated with arsenic. The concentration of arsenic in different river water samples as reported by BGS and DPHE [24] was in the range of 0.5-0.29 µg L<sup>-1</sup> and some were >0.29 µg L<sup>-1</sup>. However,

the rivers receiving industrial effluent or sewerage are reported to have greater arsenic concentration. The lowest arsenic values (i.e.  $30 \mu\text{g L}^{-1}$ ) were in River Zenne, Belgium [25], those through hundreds (up to  $556 \mu\text{g L}^{-1}$ ) were in British Columbia [26] and extremely high as  $1100 \mu\text{g L}^{-1}$  were in streams near tailing deposits of Sugar Creek, South Carolina [27].

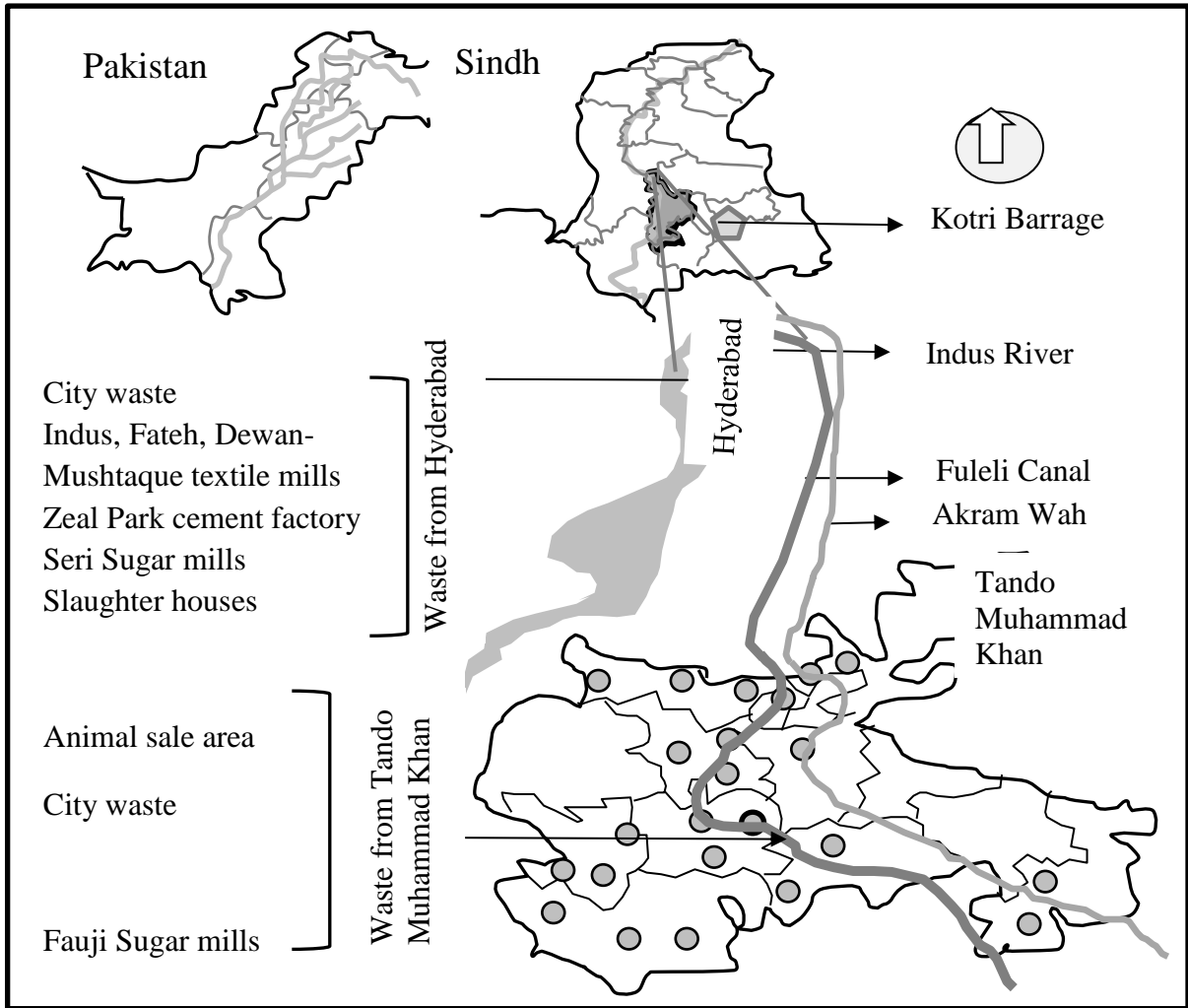
#### **Arsenic load transported to rice fields**

The net irrigation water requirements for rice crop in Pakistan vary from 1000 mm in the sub-humid to 1300 mm in the arid areas [16]. On the basis of 75% application efficiency, the gross water requirement will vary from 1300 to 1700 mm. Including the seepage of around 30% (400-550 mm), the gross irrigation requirement comes to 1700-2250 mm [16]. At the net irrigation rate of 1000 and 1300 mm  $\text{a}^{-1}$ , 0.065 and 0.084 mg  $\text{kg}^{-1}$  of arsenic can be added to soil per year. Calculated on 50 year basis, a total of 3.25 (1000 mm  $\text{a}^{-1}$ ) and 4.20 (1300 mm  $\text{a}^{-1}$ ) mg  $\text{kg}^{-1}$  of As-III can be accumulated in soils of the study area. Likewise, 0.045 and 0.058 mg  $\text{kg}^{-1}$  of As-V per year will be added to soil, respectively at the irrigation rate of 1000 and 1300 mm  $\text{a}^{-1}$ . As-V build up corresponds to roughly  $3/4^{\text{th}}$  (2.25 and 2.90 mg  $\text{kg}^{-1}$ ) of the As-III accumulation in soil over 50 years.

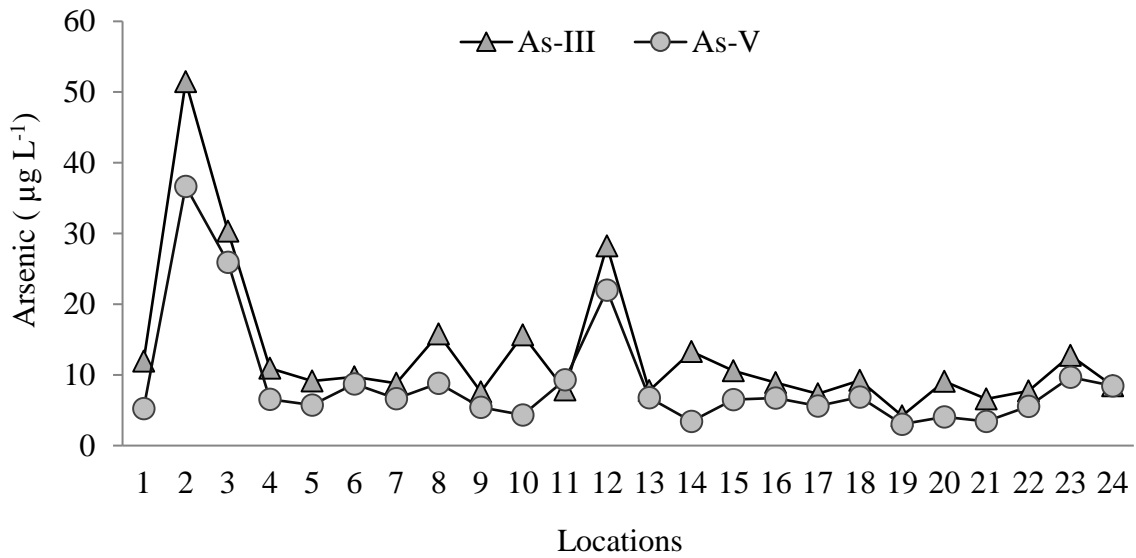
Considering the gross irrigation rate of 1700 and 2250 mm, 5.55 and 7.50 mg  $\text{kg}^{-1}$  of As-III and 3.80 and 5.05 mg  $\text{kg}^{-1}$  of As-

V can be added to soil over a period of 50 years. This comes to annual respective increase of 0.11 and 0.15 mg  $\text{kg}^{-1}$  of As-III and 0.076 and 0.101 mg  $\text{kg}^{-1}$  of As-V.

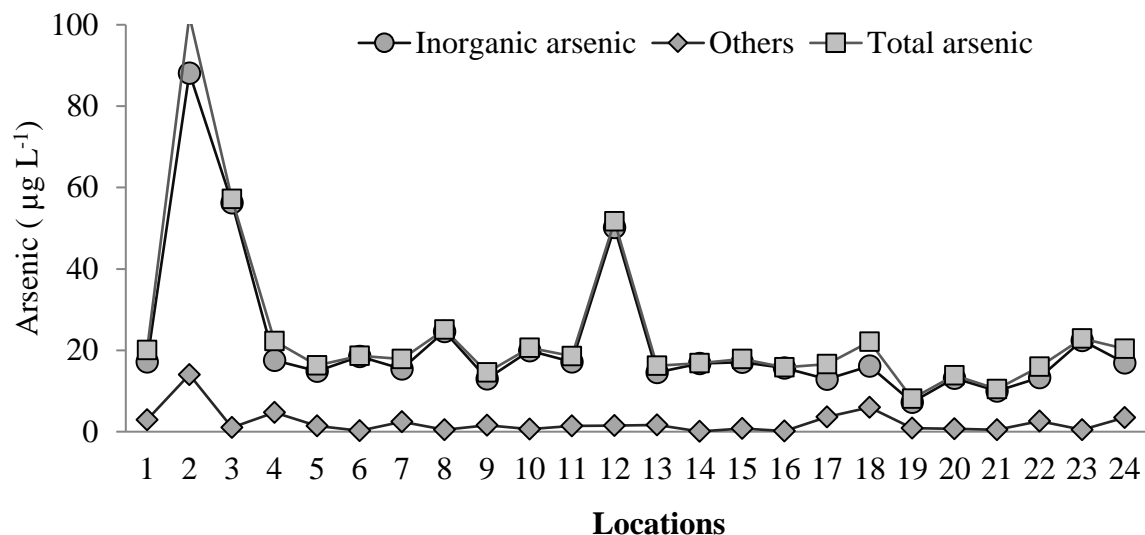
Even when arsenic load is calculated on the basis of total arsenic in water per year (Table 4), at net (0.12 and 0.16 mg  $\text{kg}^{-1}$  at 1000 and 1300 mm) and gross (0.21 and 0.28 mg  $\text{kg}^{-1}$  at 1700 and 2250 mm) irrigation rates and the existing value of arsenic in soil, it will take long time to reach the permissible limit of 50 mg  $\text{kg}^{-1}$  soil arsenic, set by FAO [15]. However, if the arsenic concentration of irrigation water keeps on rising due to increased amount of disposed waste, the rate of arsenic accumulation in soil will increase accordingly and it may cross the permissible limit sooner than that anticipated. Other than FAO, the prescribed limits suggested by Chinese Food Standard Agency (2005) and European Community (2005) are much lower (i.e. 20 and 30 mg  $\text{kg}^{-1}$  respectively), which itself is a crucial matter. The transported load to rice fields will take longer but it keeps on adding the arsenic concentration from water to soil [28]. These results are in conformity with the results of Bhattacharya *et al.* [29] and Abedin *et al.* [7], that long term addition of low concentrations of arsenic in irrigation water may results in the increase of arsenic in agricultural soils.



**Figure 1. Map of the study area in Sindh-Pakistan**



**Figure 2. Arsenite (As-III) and arsenate (As-V) in canal irrigation water associated with rice fields at Tando Muhammad Khan**



**Figure 3. Inorganic, total and other arsenic forms in canal irrigation water associated with rice fields at Tando Muhammad Khan**

**Table 1. Physico-chemical parameters in canal irrigation water associated with rice fields at Tando Muhammad Khan**

Parameter	Range	Mean± standard deviation	Permissible limits for irrigation water (FAO, 1985)
Temperature (°C)	31.10-32.71	32.42±0.55	-
pH	7.10-8.30	7.86±0.33	6.50-8.40
EC (dS m <sup>-1</sup> )	0.40-1.93	0.77±0.33	0.7-3
TDS (mg L <sup>-1</sup> )	220-960	385±161	< 450

**Table 2. Descriptive statistics of arsenic in canal irrigation water associated with rice fields at Tando Muhammad Khan**

Arsenic forms in canal irrigation water	Range	Mean	Percent contamination irrigation water FAO (1992) (50 µg L <sup>-1</sup> )
As-III (µg L <sup>-1</sup> )	4.21-51.47	13.06±10.29	4
As-V (µg L <sup>-1</sup> )	3.03-36.68	8.98±8.03	-
Total (µg L <sup>-1</sup> )	8.13-102.18	24.25±19.94	13
Others (µg L <sup>-1</sup> )	0.05-14.03	2.22±2.94	-

**Table 3. Arsenic content of different water bodies before its entrance to rice fields at Tando Muhammad Khan**

Area and type of water sample	As-III	As-V	Total arsenic	Others
	(µg L <sup>-1</sup> )			
Fuleli canal at Kotri Barrage	3.23	1.99	6.32	1.1
Akram Wah at Kotri Barrage	3.56	3.16	7.64	0.92
Wastewater of animal sale area (Bakra Piri)	16.05	9.50	26.76	1.21
Wastewater of Hyderabad city	15.60	10.90	28.78	2.28
Wastewater of industrial area in the vicinity of Indus, Fateh, Dewan-Mushtaque textile mills and Zeal Park Cement Factory	15.78	12.30	31.42	3.34
Waste water of Fauji Sugar Mills	17.5	15.00	36.24	3.74

**Table 4. Arsenic load transported from canal irrigation water to associated rice fields at Tando Muhammad Khan**

Years of irrigation	Net water usage		Gross water usage	
	1000 (mm a <sup>-1</sup> )	1300 (mm a <sup>-1</sup> )	1700 (mm a <sup>-1</sup> )	2250 (mm a <sup>-1</sup> )
<b>As-III (mg kg<sup>-1</sup>)</b>				
1	0.065	0.084	0.111	0.15
5	0.325	0.425	0.555	0.75
10	0.65	0.84	1.11	1.5
20	1.30	1.68	2.22	3.00
50	3.25	4.20	5.55	7.50
<b>As-V (mg kg<sup>-1</sup>)</b>				
1	0.045	0.058	0.076	0.101
5	0.225	0.29	0.38	0.505
10	0.45	0.58	0.76	1.01
20	0.90	1.16	1.52	2.02
50	2.25	2.90	3.80	5.05
<b>Total arsenic (mg kg<sup>-1</sup>)</b>				
1	0.12	0.16	0.21	0.28
5	0.61	0.80	1.05	1.40
10	1.21	1.60	2.10	2.80
20	2.42	3.20	4.20	5.60
50	6.05	8.00	10.50	14.00

**Conclusion**

The inorganic As-III fraction (4.21-51.47  $\mu\text{g L}^{-1}$ ) was dominant over As-V (3.03-36.68  $\mu\text{g L}^{-1}$ ). However, 3 out of 24 canal irrigation sites lying in the vicinity of Tando Muhammad Khan city were contaminated with inorganic arsenic (50.22, 56.24 and 88.15  $\mu\text{g L}^{-1}$ ), while the remaining were in the range of 7.24-24.60  $\mu\text{g L}^{-1}$ . Total arsenic following the same trend, was also high in the same 3 sites (51.72, 57.23 and 102.18  $\mu\text{g L}^{-1}$ ), remaining 21 sites were in the range of 8.13-25.1  $\mu\text{g L}^{-1}$ . The irrigation water tested at various sources before its entrance to Tando Muhammad Khan showed very low arsenic concentration emerging from the Indus River into Fuleli (6.32  $\mu\text{g L}^{-1}$ ) and Akram Wah (7.64  $\mu\text{g L}^{-1}$ ), compared to that coming from city (28.78  $\mu\text{g L}^{-1}$ ), animal shelter (26.76  $\mu\text{g L}^{-1}$ ), cement factory, and waste of textile and sugar industries (31.42  $\mu\text{g L}^{-1}$ ) at Hyderabad and Tando Muhammad Khan (36.24  $\mu\text{g L}^{-1}$ ). This shows very low or no arsenic contamination in the Indus River water (i.e. at Kotri Barrage) and that the arsenic is being added into sub-distributary canals from industrial and city waste on the way, which may

increase in the coming years. Based on net irrigation (1000-1300  $\text{mm a}^{-1}$ ) water usage in rice fields of Tando Muhammad Khan, 0.112-0.15  $\text{mg kg}^{-1}$  inorganic arsenic can be transported every year from irrigation water to rice fields. Currently, these values are way below the prescribed limits of 50  $\text{mg kg}^{-1}$  for soils. It is possible that even the low concentration of arsenic in irrigation water and even soil may lead to greater arsenic accumulation in rice plant. Therefore the future studies should include the rice plant with notably arsenic concentration in grain.

**Authors' contribution**

Conceived and designed the experiments: M Memon & I Rajpar, Performed the experiments: M Chohan, Analyzed the data: M Chohan, Contributed reagents/ materials/ analysis tools: S Akhtar, Wrote the paper: M Memon & M Chohan.

**Acknowledgment**

The study is a part of PhD research. The authors are grateful and highly acknowledge the access to Hydride Generation Unit for arsenic testing at the Department of Soil Science and Soil Water Conservation, Pir Mehr Ali Shah



University of Arid Agriculture,  
Rawalpindi.

## References

1. Zhu YG, Sun GX, Lei M, Teng M, Liu YX, Chen NC, William PN (2008). High percentage inorganic arsenic content of mining impacted and nonimpacted Chinese rice. *Environ Sci and Technol* 42: 5008-5013.
2. WHO (2003). Arsenic in drinking water. Background document for development of WHO Guidelines for Drinking-water Quality. 3.4: Estimated total exposure and relative contribution of drinking water. WHO/SDE/WSH/03.04/75,11.
3. Wattoo MH, Wattoo SFH, Tirmizi SA, Kazi TG, Bhangar MI & Iqbal J (2006). Pollution of Phulali canal water in the city premises of Hyderabad: Metal monitoring. *J Chem Soc Pak* 28: 136-143.
4. Duxbury JM, Mayer AB, Lauren JG & Hassan N (2003). Food chain aspects of arsenic contamination in Bangladesh: Effects on quality and productivity of rice. Part A: Toxic/hazardous substances and environmental engineering. *J of Environ Sci and Health* 38: 61-69.
5. Jamali MK, Kazi TG, Arain MB, Afridi HI, Jalbani N & Adil RS (2006). The correlation of total and extractable heavy metals from soil and domestic sewage sludge and their transfer to maize (*Zea mays* L.) plants. *Toxicol & Environ Chem* 88: 619-632.
6. Concon JM (1988). Inorganic and organometallic contaminants in food-stuffs. Food Toxicology Part B: Contaminants and Additives (pp. 1033-1132), Marcel Dekker, New York.
7. Abedin MJ, Cresser MS, Mehrag AA, Feldmann J & Cotter-Howells J (2002). Arsenic accumulation and metabolism in rice (*Oryza sativa* L.). *J Environ Sci Technol* 36: 962-968.
8. Hossain MF (2006). Arsenic contamination in Bangladesh—an overview. *Agric, Ecosys & Environ* 113: 1-16.
9. Nickson RT, McArthur JM, Shrestha B, Kyaw-Myint TO & Lowry D (2005). Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan. *Appl Geochem* 20: 55-68.
10. Arain MB, Kazi TG, Baig JA, Jamali MK, Afridi HI, Shah AQ, Jalbani N & Sarfraz RA (2009). Determination of arsenic levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: Estimation of daily dietary intake. *Food and Chem Toxicol* 47: 242-248.
11. Baig JA, Kazi TG, Shah AQ, Afridi HI, Kalhoro GA, Khan S, Kolachi NF, Wadhdwa SK, Shah F, Arain MB & Jamali MK (2011). Evaluation of arsenic levels in grain crops samples, irrigated by tube well and canal water. *Food and Chem Toxicol* 49: 265-270.
12. Podgorski JE, Eqani SAMAS, Khanam T, Ullah R, Shen H & Berg M (2017). Extensive arsenic contamination in high-pH unconfined aquifers in the Indus Valley. *Sci Adv* 3: e1700935.
13. Daus B, Weiss H, Mattusch J & Wennrich R (2006). Preservation of arsenic species in water samples using phosphoric acid – Limitations and long-term stability. *Talanta* 69: 430-434.
14. Chappell J, Chiswell B & Olszowy H (1995). Speciation of arsenic in contaminated soil by solvent extraction. *Talanta* 42: 323-329.
15. FAO (1992). Water quality for irrigation. In chapter miscellaneous problems, Irrigation and Drainage Paper 29-Rev. 1. FAO, Rome.
16. FAO (2003). Rice irrigation in the Near East. Current situation and prospects for improvement. (pp. 16). FAO Regional Office for Near East Cairo, Egypt.
17. FAO (1985). Water quality for agriculture. R.S. Ayers and Westcot,

- D.W. Irrigation and Drainage. Paper 29 Rev 1. (pp. 174). FAO, Rome.
18. Memon M, Soomro MS, Akhtar MS and Memon KS (2011). Drinking water quality assessment in Southern Sindh (Pakistan). *Environ Monit & Assess* 177: 39-50.
  19. Baig JA, Kazi TG, Arain MB, Afridi HI, Kandhro GA, Sarfraz RA, Jamal MK & Shah AQ (2009). Evaluation of arsenic and physico-chemical parameters of surface and ground water of Jamshoro, Pakistan. *J of Hazardous Materials* 166: 662-669.
  20. He J & Charlet L (2013). A review of arsenic presence in China drinking water. *J of Hydrol* 492:79–88.
  21. Komorowicz I and Baralkiewicz D (2016). Determination of total arsenic and arsenic species in drinking water, surface water, wastewater, and snow from Wielkopolska, Kujawy-Pomerania, and Lower Silesia Provinces, Poland. *Environ Monit Assess* 188:504
  22. Kuhn A & Sigg L (1993). Arsenic cycling in eutrophic Lake Greifen, Switzerland -Influence of seasonal redox processes. *Limnol & Oceanography* 38: 1052-1059.
  23. Asghar U, Perveen F & Alvi SK (2006). Contamination of arsenic in public water supply schemes of Larkana and Mirpurkhas Distircts of Sindh. *J Chem Soc Pak* 28: 130-135.
  24. BGS and DPHE (2001). Arsenic contamination of groundwater in Bangladesh. In: Kinniburgh D.G. and Smedley P.L. (Editors), Volume 1: Summary. British Geological Survey Report WC/00/19, British Geological Survey, Keyworth.
  25. Andreae MO & Andreae TW (1989). Dissolved arsenic species in the Schelde estuary and watershed, Belgium. *Estuarine, Coastal and Shelf Sci* 29: 421-433.
  26. Azcue JM, Mudroch A, Rosa F & Hall GEM (1994). Effect of abandoned gold mine tailings on the arsenic concentration in water and sediments of Jack of Clubs Lake, British Columbia. *Environ Technol* 15:669-678.
  27. Smedley PL & Kinniburgh DG (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem* 17: 517-568.
  28. Polizzotto ML, Lineberger EM, Matteson AR, Neumann RB, Badruzzaman ABM & Ali MA (2013). Arsenic transport in irrigation water across rice-field soils in Bangladesh. *Environ Pollut* 179: 210-217.
  29. Bhattacharya P, Samal AC, Majumdar J & Santa SC (2009). Transfer of arsenic from ground water and paddy soil to rice plant (*Oryza sativa* L.): a micro in West Bengal level study, India. *World J of Agric Sci* 5: 425-431.