Noor Ul Hassan Shar Institute of Chemistry Shah Abdul Latif University Khairpur, Pakistan noorulhassan4228@gmail.com

Abdul Raheem Shar Institute of Chemistry Shah Abdul Latif University Khairpur, Pakistan saifiraheem3863920@gmail.com

Zubeda Bhatti Department of Physics Shah Abdul Latif University Khairpur, Pakistan bhatti.zubeda@yahoo.com

Abstract-Water is a valuable compound for plants, animals, and humans. Various contaminating agents pollute it, with arsenic being one of them. Measurements of arsenic in potable water in Upper Sindh were conducted during this study. The samples were prepared by microwave-assisted digestion and analyzed by an atomic absorption spectrophotometer. A total of 240 potable water samples were collected from 8 Talukas of Upper Sindh. DMS coordinates were also recorded with the help of the Global Positioning System (GPS). The highest arsenic content of 50µg/L was observed in Garhi Khairo Taluka. The average arsenic content in water samples of all of the Talukas, except Miro Khan, was found higher than the WHO permissible limit. The 69.2% of samples were found to be contaminated by arsenic. Therefore, the water of the studied area is concluded to be in poor condition for cooking and drinking.

Keywords-arsenic; upper Sindh; atomic absorption spectrophotometer; water health risk assessment

I. INTRODUCTION

Arsenic is a metalloid with high toxicity, which can be found in the environment in geological substrata, whereas it can also be released by human activities [1]. In numerous areas, arsenic in freshwater atmosphere, due to direct release from anthropogenic and natural sources, is a severe concern [2]. The concentration of arsenic ranges from 0.5 to $5000\mu g/L$ in freshwater [3]. Four oxidation states of arsenic are observed in nature: (-3), (0), (+3) and (+5) whereas it can be found in various forms such as arsenate, arsenite, monomethylarsonic acid, dimethyl arsenic acid, trimethylarsine, arsenocholine, Ghulam Qadir Shar Institute of Chemistry Shah Abdul Latif University Khairpur, Pakistan gqadir.shar@salu.edu.pk

Shafi Muhammad Wassan Department of Community Medicine Ghulam Muhammad Mahar Medical College Sukkur Sindh, Pakistan wassanshafi1975@gmail.com

> Abida Ali Department of Computer Science Shah Abdul Latif University Khairpur, Pakistan abida.ali@mckru.edu.pk

arsenobetaine, arsenosugras, etc. Organic arsenic is less poisonous than inorganic arsenic, while pentavalent arsenic is less toxic than its trivalent state [4]. Arsenic is accumulated in soil through human activities like fuel utilization, mining, smelting of arsenic ores, manufacture of arsenic–based compounds, and use of arsenic–based pesticides [5, 6]. Biomethylation mechanism of micro-organisms and use of organo-arsenical pesticides are responsible for organic arsenic in natural water systems [7]. Higher concentrations of arsenic in groundwater of countries like Italy, Vietnam, Bangladesh, West Bengal, Hungary, China, Mexico, Chile, and Argentina have been observed [8].

Water resources are exploited because of the continuous development of global population. Arsenic and heavy metal contamination of water sources are often found to be in extremely critical state [9]. These pollutants find their ways in surface and groundwater sources due to their high mobility. There are various groundwater and surface water sources [10]. When compared to surface water, groundwater is more secure regarding heavy metals and microbes [11]. Therefore, most people use groundwater for drinking purposes [12], although a lot of research has been conducted on groundwater containing heavy metals [13]. About 100 million people of Southeast Asia were found to be at high risk of arsenic toxicity [14]. There are two main ways of arsenic accumulation in the human body, taking arsenic polluted potable water and consuming arsenic contaminated food [15]. Stomach toxicity, brain, kidney, and liver cancers, and skin lesions may be the results of chronic

Corresponding author: Abdul Raheem Shar

effects of arsenic. Due to its toxicity, WHO and USEPA have reduced the threshold limit of arsenic from 50 to $10\mu g/L$ in 2001 [16].

To the best of our knowledge, in the 8 Talukas of upper Sindh that constitute the studied area, arsenic contamination and health risk assessment in potable water have not been conducted. The present work aimed to identify arsenic contamination and its potential health risk assessment in upper Sindh keeping in view the public, anthropogenic inputs and geology.

II. MATERIALS AND METHODS

A. Study Area

The weather of upper Sindh is moderate in winter and extremely hot in summer. The area is commonly considered as a hot arid zone. The lowest and the highest temperatures recorded are -3.9°C and 52.8°C respectively. In the season of monsoon from July to September the rainfall is not sufficient. The average recorded annual rainfall is 122.5mm and the air is generally dry. Upper Sindh lies from 27°56' to 28°27' N and from 68° to 69°44' E covering an area of about 6,790km². In its surroundings, Thar Desert is located on the eastern side, Bahurai range in west, Kherthar range in south west and Suleman range in the north. At the south eastern side of Jacobabad. Indus River flows from north to south and besides the Bolan River there are various canals and streams at the western and northern sides. There are parts of Baluchistan highlands at northern, western, and south western areas and as a result, non-perennial streams are found towards the province of Sindh [17].



Fig. 1. Hand pumps in the study area.

B. Chemicals and Reagents

Reagents bought from Merck (Darmstadt, Germany) along with de-ionized water were used for arsenic solution preparation.

C. Sampling

In order to get groundwater samples it is necessary to run hand pumps at least for 5 minutes to eliminate insoluble impurities and sand particles and to get depth water of required elemental amounts [18]. Water used for drinking was obtained from hand pumps whose depth was varied from 30 to 70 feet. Plastic 1500 mL bottles were used to collect the water samples. Eight Talukas of upper Sindh were selected to be sampled. The coordinates were recorded with the help of a GPS device. In total, 240 potable water samples were collected from 8 Talukas of upper Sindh. After collection, the water samples were transported immediately to the laboratory. Practical investigation of arsenic was conducted in the laboratory and its quantity was measured with the help of a calibration graph.

D. Instrumentation

To measure the arsenic contamination from potable water, the technique of Atomic Absorption Spectrophotometer (Perkin-A 700) was used along with Mercury Hydride System (MHS–15). It is a precise and simple method of analysis of metals found in various samples [19].

E. Microwave Digestion Method

PTFE flasks were taken and 500mL of water samples were kept in them. After closing tightly, the flasks were subjected to microwave radiation in stopped up vessel microwave digestion using Milestone Ethos D model (Sorisole-Bg, Italy). The digestion plan of microwave oven was 100W for 2min, 250W for 6min, 400W for 5min, 550W for 8min, and ventilation for 8min. After the cooling, the content of the flask was diluted with 0.2M nitric acid to 10mL. The same procedure was followed to prepare the reagent blank. The advantage of microwave digestion method is that it takes less time to digest water samples and the possibility of evaporation of elements is less, therefore more precise extraction of elements from samples can be accomplished as compared to conventional digestion methods. Less acid is used for digestion as well [20].

III. RESULTS AND DISCUSSION

More than 40% of the population of Pakistan suffers from arsenic contamination in potable water. More than 20% of the people of Punjab suffer from arsenic contamination in surface or groundwater sources, with the problem becoming bigger in industrial zones [21-24]. According to our results, the highest concentration of 50µg/L of arsenic was obtained in Garhi Khairo Taluka and the minimum of 3µg/L was found in samples from Ubauro, Tangwani, Kambar, and Miro Khan Talukas. The mean arsenic content in all Talukas except Miro Khan was higher than the WHO permissible limit. In Daharki and Kambar Talukas, 80% of groundwater samples were contaminated by arsenic, in Kashmore and Garhi Khairo 86.7%, and in Ubauro, Tangwani, Thul, and Miro Khan the contamination percentage was 70%, 73%, 56.7%, and 20% respectively (Table I). Water quality is worse in heavily populated regions of Pakistan such as Peshawar, Lahore, Karachi, Shaheed Benazirabad [49] and other cities and towns. The groundwater of upper Sindh is also contaminated and not safe for drinking due to its high arsenic contamination. Some reported cities of Pakistan with high arsenic content in groundwater are shown in Table II. Arsenic concentration in various countries is given in Table III. Descriptive statistics such as, minimum, maximum, mean and standard deviation of arsenic in potable water of upper Sindh are given in Table IV.

Daharki	Ubauro	Kashmore	Tangwani	Garhi Khario	Thul	Kambar	Miro Khan
5	10	9	21	17	38	11	9
11	12	12	7	16	13	3	6
14	20	12	9	12	12	16	4
11	18	13	18	11	8	21	5
5	19	10	19	4	7	12	6
10	26	14	16	9	8	3	5
11	18	11	12	20	5	15	18
14	15	10	20	13	16	21	17
15	12	12	33	12	9	18	16
5	24	15	24	12	8	26	17
16	37	12	37	4	8	34	7
17	25	16	10	17	6	49	5
13	38	18	8	22	13	26	3
15	25	18	6	13	18	11	6
5	3	13	9	4	9	10	7
19	14	15	14	16	8	16	9
20	13	19	16	22	12	15	7
17	11	9	11	19	18	11	9
14	17	14	17	27	15	10	6
13	9	13	25	35	23	3	15
18	6	13	39	50	31	8	6
17	5	14	25	27	46	19	7
10	7	15	3	12	23	12	15
13	9	17	9	11	8	11	7
11	18	24	22	16	7	15	10
12	19	27	20	13	12	12	5
14	18	17	19	34	9	33	6
13	20	17	26	25	30	24	7
13	5	21	18	20	21	19	5
27	6	12	15	30	16	29	9

TABLE I. ARSENIC CONCENTRATION $(\mu g/L)$ in the studied eight talukas of upper sindh

 TABLE II.
 CONCENTRATION OF ARSENIC IN DIFFERENT CITIES OF PAKISTAN

Province	Area	As (µg/L)	References	
	Sajawal	15.3	[25]	
	Ghorabari	50	[26]	
	MirpurSakro	80	[26]	
	Ketibandar	5-25	[27]	
6° 11	Khairpur	0.24-315.6	[28]	
Sindh	Gambat	0.01-126	[29]	
	Shaheed Benazirabad	10-200	[30]	
	Dadu	8-67	[31]	
	Thatta	10-200	[32]	
	Jamshoro	13-106	[33]	
	Sheikhupura	5-76	[34]	
D	Rahimyar Khan	20-500	[35]	
Punjab	Muzffargarh	0.01-900	[36]	
	Dera Gazi Khan	1–29	[37]	
Balochistan	Sibi	0.3-3.5	[38]	
Duroemstan				

 TABLE III.
 ARSENIC CONCENTRATION IN VARIOUS COUNTRIES

Country	Concentration (µg/L)	Reference
India	44	[39]
China (Shanxi)	1932	[40]
Afghanistan	100	[41]
Taiwan	1800	[42]
Greece	> 20	[43]
Bangladesh	398	[44]
Veitnam	3100	[45]
Nepal	260	[46]
Cambodia	3500	[47]
Inner Mongolia, China	4000	[48]

 TABLE IV.
 DESCRIPTIVE STATISTICS OF ARSENIC IN POTABLE

 WATER OF UPPER SINDH

Taluka	Ν	Min	Max	Mean	Std. deviation
Daharki	30	5	27	13.3	4.78
Ubauro	30	3	38	16.0	8.74
Kashmore	30	9	27	14.7	4.18
Tangwani	30	3	39	17.6	8.85
Garhi Khario	30	4	50	18.1	10.11
Thul	30	5	46	15.2	10.00
Kambar	30	3	49	17.1	10.11
Miro Khan	30	3	18	8.5	4.32

Shar et al.: Health Risk Assessment of Arsenic in the Drinking Water of Upper Sindh, Pakistan

A. Pearson Correlation Coefficient

The Pearson correlation of the potable water of the 8 talukas of upper Sindh is shown in Table V. Positive correlation was observed among Garhi Khairo and Daharki (0.483). Arsenic in potable water of Thul and Garhi Khairo also showed positive correlation of 0.491, whereas the water of the Kambar and Ubauro Talukas also displayed positive correlation of 0.415. Negative correlation of arsenic in drinking water was found among Talukas Thul and Ubauro. All relations were observed significant at the level of 0.05, and 0.1 respectively.

B. Human health risk assessment

Equation (1) was used to estimate the total arsenic intake [33]:

$$ADI = \frac{Cw \times Di}{BW} \quad (1)$$

Body weight (BW) and daily water intake for common people were supposed to be 65kg and 3 to 3.5L respectively. The results of the Average Daily Intake (ADI) are given in Table VI. ADI values at alarming levels were found in the water of all Talukas of upper Sindh with the exception of Miro Khan. The values ranged from 0.46 to $0.97\mu g/day$. Comparatively, Tangwani, Garhi Khairo, and Kambar Talukas showed higher ADI values. Various problems may be caused due to high ADI values such as diabetes, cardiovascular problems, hypertension, black foot disease, keratosis, bladder and lung cancer, and skin lesions [31] (Tables VI, VII).

TABLE V. CORRELATION COEFFICIENT OF ARSENIC IN GROUNDWATER OF DIFFERENT UPPER SINDH TALUKAS

	Daharki	Ubauro	Kashmore	Tangwani	Garhi Khario	Thul	Kambar	Miro Khan
Daharki	1							
Ubauro	-0.097	1						
Kashmore	0.057	0.150	1					
Tangwani	0.097	0.023	-0.063	1				
Garhi Khario	0.483**	-0.308	0.040	0.319	1			
Thul	0.095	-0.432*	-0.132	0.262	0.491**	1		
Kambar	0.306	0.415*	0.092	0.116	-0.004	-0.197	1	
Miro Khan	-0.136	-0.217	-0.300	0.159	-0.030	-0.029	-0.074	1

TABLE VI. AVERAGE DAILY INTAKE OF ARSENIC FROM DRINKING WATER OF DIFFERENT UPPER SINDH TALUKAS

Daharki	Ubauro	Kashmore	Tangwani	Garhi Khario	Thul	Kambar	Miro Khan
0.27	0.54	0.48	1.13	0.92	2.05	0.59	0.48
0.59	0.65	0.65	0.38	0.86	0.70	0.16	0.32
0.75	1.08	0.65	0.48	0.65	0.65	0.86	0.22
0.59	0.97	0.70	0.97	0.59	0.43	1.13	0.27
0.27	1.02	0.54	1.02	0.22	0.38	0.65	0.32
0.54	1.40	0.75	0.86	0.48	0.43	0.16	0.27
0.59	0.97	0.59	0.65	1.08	0.27	0.81	0.97
0.75	0.81	0.54	1.08	0.70	0.86	1.13	0.92
0.81	0.65	0.65	1.78	0.65	0.48	0.97	0.86
0.27	1.29	0.81	1.29	0.65	0.43	1.40	0.92
0.86	1.99	0.65	1.99	0.22	0.43	1.83	0.38
0.92	1.35	0.86	0.54	0.92	0.32	2.64	0.27
0.70	2.05	0.97	0.43	1.18	0.70	1.40	0.16
0.81	1.35	0.97	0.32	0.70	0.97	0.59	0.32
0.27	0.16	0.70	0.48	0.22	0.48	0.54	0.38
1.02	0.75	0.81	0.75	0.86	0.43	0.86	0.48
1.08	0.70	1.02	0.86	1.18	0.65	0.81	0.38
0.92	0.59	0.48	0.59	1.02	0.97	0.59	0.48
0.75	0.92	0.75	0.92	1.45	0.81	0.54	0.32
0.70	0.48	0.70	1.35	1.88	1.24	0.16	0.81
0.97	0.32	0.70	2.10	2.69	1.67	0.43	0.32
0.92	0.27	0.75	1.35	1.45	2.48	1.02	0.38
0.54	0.38	0.81	0.16	0.65	1.24	0.65	0.81
0.70	0.48	0.92	0.48	0.59	0.43	0.59	0.38
0.59	0.97	1.29	1.18	0.86	0.38	0.81	0.54
0.65	1.02	1.45	1.08	0.70	0.65	0.65	0.27
0.75	0.97	0.92	1.02	1.83	0.48	1.78	0.32
0.70	1.08	0.92	1.40	1.35	1.62	1.29	0.38
0.70	0.27	1.13	0.97	1.08	1.13	1.02	0.27
1.45	0.32	0.65	0.81	1.62	0.86	1.56	0.48

Note: Safe arsenic daily intake in water is 0.66µg/day

Taluka	Mean (µg/L)	ADI Mean (µg/day)
Daharki	13.3	0.72
Ubauro	16	0.86
Kashmore	14.7	0.79
Tangwani	17.6	0.95
Garhi Khairo	18.1	0.97
Thul	15.2	0.82
Kambar	17.1	0.92
Miro Khan	8.5	0.46

 TABLE VII.
 MEAN ADI OF ARSENIC IN POTABLE WATER OF THE UPPER SINDH TALUKAS

IV. CONCLUSION

From the results obtained from the present work, it can be concluded that the groundwater of upper Sindh is unfit for drinking due to the presence of arsenic in high amounts. With the exception of Miro Khan where only 20% of water samples were found to be contaminated, the potable water of the Talukas was found highly contaminated due to the existence of arsenic concentration at alarming levels. Contaminated water may cause various health hazards. Therefore, it is suggested to the government of Sindh to pay special consideration to the matter. It is also recommended that awareness among farmers must be increased to use chemicals, particularly pesticides, carefully. Also, the government should provide safe drinking water by installing Reverse Osmosis (RO) plants in areas where people are using unsafe water for drinking and cooking.

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