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Analytical Investigation of Arsenic and Iron in hand pump and tube-well groundwater of Gambat, Sindh, Pakistan

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ABSTRACT

Contamination of drinking water especially with heavy metals is now a major issue from both the public health and the environmental health perspectives. In present work we are reporting a multivariate study for the concentrations of Arsenic and Iron in groundwater n=334 collected from Gambat, Khairpur, Sindh, Pakistan during year 2008. The analysis was performed using Hydride Generator Atomic Absorption Spectrometry (HG-ASS) Perkin Elmer A-100 coupled with MHS-15. Arsenic and Iron were evaluated in hand pump and tube well water sample with detection limit 0.02µg$L^{-1}$and 01µgL^{-1} respectively. The level of arsenic was found in hand pump and tube well water ranged from <0.01 to 126µgL^{-1} and <0.01-38 µgl^{-1} respectively. While level of Iron was found in the rage of <0.004-1.6mgL^{-1} and <0.004-1.5mgL^{-1} in hand pump and tube well groundwater respectively. It has observed that in most of the samples level of these both elements were above than the maximum permissible level of World Health Organization.

Keywords: Arsenic, Groundwater, Gambat

1. INTRODUCTION

Water is an essential component for survival of life on earth, which contains minerals, important for humans as well as for earth and aquatic life. If water become contaminated by organic and inorganic hazardous materials especially with heavy metals that develop a major problem for both the public health and the environmental aspects. Pakistan belongs to an in developing country also facing major problem of water pollution due to poor management for disposal of Industrial influent and domestic waste[1]. Among various types of contamination Arsenic pollution is one of a major threat for in developing countries of south East Asia[2-5]. Arsenic is an element that occurs naturally in rocks and soil. The World Health Organization (WHO), the Department of Health and Human Services (DHHS), and the Environmental Protection Agency (EPA) have determined that inorganic arsenic can cause cancer in humans[6]. Several studies have shown that inorganic arsenic can increase the risk of lung cancer, skin cancer, bladder cancer, liver cancer, kidney cancer, and prostate cancer[7-8]. Besides this non carcinogenic effect are also attributed to arsenic due to its contamination in groundwater includes: thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhea, numbness in hands and feet, partial paralysis, blindness etc[9].

Arsenic contamination in groundwater and its risk assessment to the human health from various countries of the world has also been reported in literature including Bangladesh, West Bengal, India, USA, China, Canada, Mexico, Argentina, Vietnam, Mongolia, Germany, Romania and Thailand[10-13]. Similarly Pakistan is also facing serious arsenic pollution in its groundwater in various places. The aim of present study was to evaluate possible contamination of arsenic and iron in groundwater of Gambat, Sindh Pakistan by using sophisticate instrument and followed by International laboratory protocol. So far in study area the analysis of arsenic in groundwater has not been conducted by any organization. Thus, the evaluation of arsenic in groundwater and correlation with other trace toxic element was the need of the time. It becomes more important to investigate the possible sources of arsenic pollution by using multivariate techniques. i.e. temperature, pH, and concentration of other heavy metals. As well as examine the effect of poisons in different sampling sites, in view to find out the information about similarities and dissimilarities among the different sampling sites, according to arsenic contamination levels.

2. EXPERIMENTAL

2.1 *Description of study area*

Gambat is a Taluka city of Khairpur District lying south of the Indus River the east by India and positioned between **(27°21'6"N and 68°31'22"E).** It is located in northern Sindh and it is a subtropical region, mostly hot in summer and cold in winter. The temperature ranged from 4-46 ^{0}C with >250 mm average rainfall[14]. Most of the villages are located on fertile agricultural land in the flood plain of the Indus River but due to poor management of the available water, the quality of drinking water is gradually deteriorating day by day. There are many possible source of pollution of these trace and toxic metal but it is assumed that, the agricultural/industrial pollution is a main source in surface and groundwater[15].

2.2 *Sample collection, transportation, preservation and Storage*

Almost 334 water samples were taken from different villages on the basis of the Union Council followed by ISO sampling method 5667 of sampling protocol for Arsenic analysis (As-III and As-V), for statistical significance the

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cluster sampling is adopted. Groundwater samples were collected from sampling points of Taluka Gmabat, Khairpur, Pakistan with the help of Global Positioning System (GPS) in 2008. Samples were collected from hand pumps, and tube well by using a procedure given below.

The collection of samples was performed by using polypropylene bottles of 05-1.0 L capacity. These bottles were soaked in 10% nitric acid for 24 h and rinsed with ultrapure water. For each bottle, water sample was run at fast flow for five minutes; a durable label (waterproof) and indelible ink were used to mark the sample bottle for identification of the sample location. All sample bottles were kept in polyethylene plastic bags.

Sample were collected from >35 feet depth of hand pump and >80 feet of tube well water. In the field, we measured water temperature and pH by thermometer, pH meter (781-pH meter Metrohm) respectively. Preservation of samples and field blank were performed in the field as well as in the laboratory. Preservation involves the addition of 10% HNO_3 to bring the sample to pH <2. For samples found at neutral pH, approximately 5 mL of 10% HNO_3 per litter was added. The preserved samples were stored for a minimum of 48 hours at 0-4 ^{0}C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls. With each sample set, the method blank and an ongoing precision and recovery (OPR) were also preserved in the same way as the sample.

2.3 *Reagents and glassware*

Ultrapure water obtained from ELGA Lab water System (Bucks, UK) was used throughout the work. Concentrated HCl, and HNO_3 were analytical reagent grade from Merck (Darmstadt, Germany). Argon gas with 99.99% purity was used as sheath gas for the atomizer and for internal purge. Solution Sodiumtetrahydroborate was prepared by dissolving $NaBH_4$ powder (Across Organics, New Jersey, USA) in 0.5 M KI. Standard solutions of all elements under study were prepared by dilution of certified standard solutions (1000 mg L^{-1}, Fluka Kamica, Buchs SG and Switzerland) of corresponding metal ions. Calibrations were prepared for each analytical session using stock standard solution of each metal.

2.4 *Water analysis*

Samples of hand pump water and tube-well water collected from different sites were filtered through 0.45 μm filter paper with the help of vacuum pump and stored at 4 °C until processing and analysis. Total Arsenic and other metals were determined by Perkin Elmer AA-100 Atomic Absorption Spectrometer equipped with a deuterium background corrector and a Mercury Hydride Generator System (MHS-15), Perkin Elmer Corp. Perkins Elmer (Shelton, CT, USA) was used for As determination only.

2.5 *Analysis Procedure*

For As determination a second dilution was made by taking different aliquots of the master stock sample solutions and diluting with 1.5% of HCl. Arsine gas was generated and solutions were swept by Argon gas stream into pre-heated quartz tube atomizer installed over a burner with lean, blue air-acetylene flame. Analysis was performed in peak height mode to determine absorbance. A blank extraction (without sample) was carried out through out the complete procedure. The concentrations were obtained directly from calibration graphs after correction of the absorbance for the signal, from an appropriate reagent blank. All experiments were conducted at room temperature (30 ^{0}C) following the well-established laboratory protocols. To stabilize the HG-AAS system the acidic blank is often followed through the sample inlet tube for five or ten min although the longer this goes on, the more acidic waste is produced. Statistical analyses were performed using computer programme Microsoft Excel 2000 (Microsoft corp. Redmond, WA).

2.6 *Percentage recovery test*

Efficiency of the method was checked by standard addition method. The triplicate samples of water spiked with known amount of arsenic standard prior to analysis were prepared. Sample blank also prepared and was run after each sample. Each result value is mean of three independent batches prepared in triplicate and each sample analysed at least twice. The matix of standards and sample solution was same by using 0.5% V/V hydrochloric acid. The percentage recovery test was obtained 97-99% in range.

3. RESULTS AND DISCUSSION

For convenience in description, groundwater samples were grouped into two categories according to depth: hand pump samples (HP, *n* = 230) from 35 to 40`feet depth and tube-well samples (TW, *n* = 104) from 80 to 100 feet depth.

The pH is one of the most important parameters to test the water quality and it is also a useful test for interpretation of water chemistry. The pH of both hand pump and tube-well water samples were found neutral and it was within the WHO recommended values.

Data obtained from analysis indicated that level of As and Fe were found high in both HP and TW samples. The pH and temperature of all samples were found within the safe limit of WHO. Mean concentration of As in HP and TW water was 26.6μg`L^{-1} and 11.1 μg L^{-1} comparatively above than WHO recommended limit (10μgL^{-1}). It could be further discussed that samples of TW groundwater show significantly low mean concentration of arsenic as compared to sample of HP water. This may be due to greater depth of tube-well but in case of Fe, it shows no significant difference between HP and TW water samples. Ranges of analytical data of various elements from HP and TW water of different sampling sites are given in Tables 1,2. It has been observed that As contents from HP water of sampling site Gamabt-I show the mean value 9.6 µg L^{-1} and raged from 0.24 to 46µg L^{-1} relatively lower than sampling site of Gambat-II the mean value 16.3 µg L^{-1} and ranged from 0.12-126 µg L^{-1}. Highest arsenic concentration was noted in hand pump groundwater sample from sampling site Agra and Khemtia with mean value 45 and 43 µg L^{-1} ranged from 0.46-81 µg L^{-1} and 0.25-126 µg L^{-1} respectively. Sampling site Bhelaro and Kamal Dero shows the mean value of As 30.4 and 38.4 ranged from 0.01-55 and 0.23-111 µg L^{-1} slightly have lowest mean concentration. Groundwater samples from HP of Khura and Jado-Wahan shows the As mean value 11.4 µg L^{-1} ranged from 0.25-101µg L^{-1} and 20 µg L^{-1} ranged from 0.5-75 µg L^{-1} respectively. Sampling point No. 55a and 194a shows highest As value 126 and 111µg L^{-1}. Figure 1 represented graphically the level of arsenic in HP groundwater from various sampling sites.

Table-1. Ranges of analytical data of various parameters from hand pump and tube-well groundwater in Gambat, Sindh, Pakistan

		Gambat-I			**Gambat-II**			**Khemtia**			**Bhelaro**		
		Min	***Max***	***Mean***	***Min***	***Max***	***Mean***	***Min***	***Max***	***Mean***	***Min***	***Max***	***Mean***
T (^{0}C)	***HP***	28	37	32.71	31	36	32.7	28	36	32	31	35	33.8
	TW	31	32	32.8	30	36	32.5	31	35	32.8	31	36	33.5
pH	***HP***	6.8	7.2	7.0	6.8	7.5	7.2	6.8	7.3	7.1	6.8	7.3	7.1
	TW	7.0	7.5	7.2	7	7.2	7.1	7	7.4	7.2	6.6	7.5	7.0
As µgL^{-1}	***HP***	0.24	46	9.6	0.12	126	16.3	0.25	126	43	0.01	55	30.4
	TW	0.01	23	10.2	0.06	23	11.6	0.05	10	5.3	0.05	23	09
Fe mgL^{-1}	***HP***	0.004	1.2	0.27	0.061	1.4	0.3	0.004	0.48	0.18	0.12	1.4	0.38
	TW	0.06	0.48	0.22	0.005	0.31	0.13	0.1	1.5	0.48	0.12	1.2	0.29

HP = hand pump water, TW= Tube well water

Table-2: Ranges of analytical data of various parameters from hand pump and tube-well groundwater in Gambat, Sindh, Pakistan

		Khura			**Agra**			**Jado-W**			**Kamal-D**		
		Min	***Max***	***Mean***	***Min***	***Max***	***Mean***	***Min***	***Max***	***Mean***	***Min***	***Max***	***Mean***
T (^{0}C)	***HP***	30	36	32.6	28	34	31.2	31	36	33.2	30	33	31.7
	TW	30	36	32.7	30	35	32.4	31	35	32.6	30	34	32.4
pH	***HP***	6.8	7.2	7.1	6.6	7.4	7.0	7	7.6	7.1	6.7	7.2	7.0
	TW	6.8	7.5	7.3	6.9	7.5	7.3	7.1	7.7	7.4	7.2	7.5	7.4
As µgL^{-1}	***HP***	0.25	101	11.4	0.46	81	45	0.5	75	20.0	0.23	111	38.3
	TW	.03	32	10.3	0.09	32	11.8	0.06	23	11.5	0.82	38	17.3
Fe mgL^{-1}	***HP***	0.08	1.2	0.24	0.004	1.31	0.27	0	1.6	.32	0.12	1.21	0.28
	TW	0.12	0.36	0.19	0.004	0.4	0.16	.21	1.35	0.61	0.11	1.5	0.4

HP = hand pump water, TW = Tube well water

Table-3: Comparison of the collected data of the groundwater samples in Gambat, Sindh, Pakistan with the recommended WHO values

	Recommended values WHO(2004)	**Hand pump n=230[a]**			**Tube well n=104[a]**		
		Min	***Max***	***Average***	***Min***	***Max***	***Average***
T (^{0}C)	(25-39 ^{0}C)	28	37	32.3	30	36	32.7
pH	(6.5-8.5)	6.6	7.6	7.1	6.6	7.7	7.2
(As µg L^{-1})	(10 µgL^{-1})	0.01	126	26.6	0.01	38	11.1
Fe (mg L^{-1})	(0-0.3mgl^{-1})	0.004	1.6	0.28	0.004	1.53	0.28

[a] No. of samples

Table-4: Percentage of samples contaminated by Arsenic and Iron.

Sr. No	**Gambat-I**		**Gambat-II**		**Khemtia**		**Bhelaro**		**Khura**		**Agra**		**Jado-W**		**Kamal-D**	
	HP	***TW***	***HP***	***TW***	***HP***	***TW***	***HP***	***TW***	***HP***	***TW***	***HP***	***TW***	***HP***	***TW***	***HP***	***TW***
	n=20	*n=13*	*n=20*	*n=13*	*n=21*	*n=13*	*n=18*	*n=13*	*n=35*	*n=13*	*n=26*	*n=13*	*n=46*	*n=13*	*n=44*	*n=13*
As	20	15	40	20	60	23	72	25	17	13	84	38	41	13	66	30
Fe	15	15	10	8	14	10	16	12	5	3	25	20	16	12	20	18

Comparison study of As in groundwater with World Health Organization limit (10 µg L^{-1}) is indicated that in both HP and TW samples the level of As is high 26.6 µg L^{-1} and 11.1 µg L^{-1}.It can be further seen from Table-3 that average value of Fe, pH and Temperature are within the safe limit as given by WHO. While highest level of Fe was noted in HP 1.6mg $L^{-1}$and TW 1.54mg L^{-1} relatively above than permissible limit of WHO (0.3mg L^{-1}).

Percentage study of samples contaminated by As is given in Table 4. The data show that 84% of samples from sampling site Agra were above the level of the WHO recommended guidelines and therefore are chemically unfit for human consumption. Percentage of samples contaminated by As is represented in graphically in figure 2 indicated that following sample sites Agra, Bhelaro, Kamal Dero, Khemtia, Jado Wahan, Gambat-II, Gambat-I and Khura shows 84%, 72%, 66%, 60%, 41%, 40%, 20% and 17.8% respectively.

Correlation of As in HP for different sampling sites are given in table 5 indicated significant positive correlation between sampling sites Bhelaro with Khemtia r=0.467, Bhelaro with Gambat r=0.33, Khemtia with Agra r=0.336, Khemtia with Jado-Wahan r=0.30, Bhlero with Jadowahan r=0.31 and Kamal Dero with Jadowahan r=0.35 while negative correlation is observed between sampling sites Khura with Agra r=0.421.

Table-5: Correlation of Sampling sites on the basis of As level in hand pump water from different sampling sites in Gambat, Khairpur, Sindh, Pakistan

	Gambat-I	Gambat-II	Khemtia	Bhelaro	Khura	Agra	Jado-Wahan
Gambat-II	0.240						
Khemtia	0.176	-.067					
Bhelaro	0.331	.072	0.467(*)				
Khura	0.234	0.106	-.228	.067			
Agra	-.194	.128	0.336	0.104	-.421(*)		
Jado-W	-.044	-.078	0.300	0.310	-.250	0.015	
Kamal-D	-.094	-.117	0.191	-.071	0.111	0.038	0.352

* Correlation is significant at the 0.05 level (2-tailed).

Table-6: Correlation of Sampling sites on the basis of As level in tube well water from different sampling sites in Gambat, Khairpur, Sindh, Pakistan

	GambatI	GambatII	Khemtia	Bhelaro	Khura	Agra	Jado-W
GambatII	.354						
Khemtia	.344	-.124					
Bhelaro	-.145	-.062	.247				
Khura	-.071	.008	0.433	.319			
Agra	-.399	-.439	.059	-.091	-.199		
Jado-W	0.268	0.459	-.400	0.403	-.175	-.517	
Kamal-D	0.266	0.395	-.246	-.525	-.466	.006	0.105

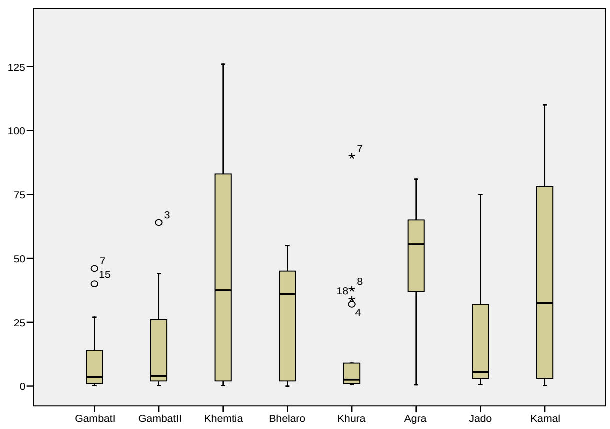

Fig-1: Level of Arsenic in HP groundwater samples of various sampling sites

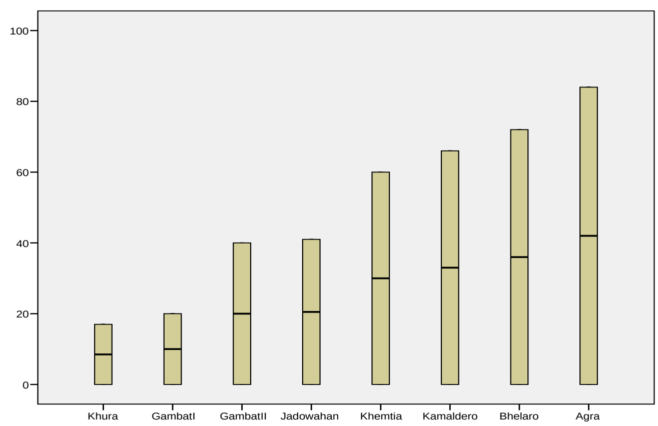

Fig-2: Percentage of samples contaminated by Arsenic

Correlation study of As in TW sample of different sampling site are given in table 6 indicated significant positive correlation between Gambat-II with Jadowahan r=0.46, Khemtia with Khura r=0.43, Bhelaro with Jadowahan r=0.40 and Kamaldero with Gambat-II r=0.39. While good negative correlation has been observed between Bhelaro and Kamaldero r=0.52.

It has been further discussed that in study area, groundwater (HP and TW water) is being used for drinking, cooking and personal hygiene. Present study show that in many area the concentration of As and Fe is higher than the recommended safe limits of WHO. So this poses a serious problem for the local Government to protect human health from As threat. There are various form of arsenic pollution in water[15]. Arsenic can combine with other elements to make chemicals used to preserve wood and to kill insects on cotton and other agricultural crops. High arsenic levels may come from certain fertilizers, animal feedlots, industrial waste and herbicides[16]. Although As status in Gambat Pakistan, is at dangerous position, therefore million of people are at arsenic risk so necessary preventive measure should be adopted to minimize the risk level in study area.

4. CONCLUSION

The evaluation of total arsenic and Iron contents in hand pump groundwater (230samples) and tube-well groundwater (104 samples) of Gambat, Sindh, Pakistan, were performed in order to be aware about the arsenic pollution in the study area. It is concluded that arsenic concentration in most of HP and TW samples was higher than the permissible limits proposed by WHO. The multivariate technique, cluster analysis of understudy sites clearly showed the high, medium and less polluted sites for hand pump and tube-well groundwater. In general, the hand pump groundwater the level of arsenic was high than that of tube-well water, possibly due to high depth. To reduce the impact of arsenic on human health there is now a need to have treatment systems to remove arsenic from drinking water. However, a more detailed understanding of local sources of arsenic and mechanisms of arsenic release is required. More extensive studies will be required for building practical guidance on avoiding and reducing arsenic contamination especially in groundwater.

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