

International Journal of Biosciences | IJB | ISSN: 2220-6655 (Print) 2222-5234 (Online) http://www.innspub.net Vol. 16, No. 1, p. 394-400, 2020

RESEARCH PAPER

OPEN ACCESS

Risk assessment of arsenic in groundwater of Jacobabad City

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Key words: Arsenic, Jacobabad city, WHO limit, Atomic absorption spectrophotometer

http://dx.doi.org/10.12692/ijb/16.1.394-400

Article published on January 30, 2020

Abstract

Water is vital constituent for survival of existence on earth, which contains minerals, essential for humans as well as for earth and aquatic life. Water is being polluted due to industrialization, with varying polluting agents, arsenic (As) contamination is one of them. A comprehensive study was carried out for the determination of Arsenic in groundwater of Jacobabad city using microwave-assisted digestion followed by atomic absorption spectrometry (AAS) coupled with mercury Hydride generation system (MHS-15). For that purpose, a total of 98 ground water samples were collected from 07 union councils (UCs) of the Jacobabad city on global position (GPS) method. Results revealed that maximum concentration of As was found (22.0) μ g/L in UC-6, (15) μ g/L in UC-1 and in UC-3, (13) μ g/L in UC-4 and in UC-7, while (12) μ g/L in UC-5 and in UC-2 respectively. The minimum and maximum mean concentration of Arsenic was found (3.4) μ g/L and(14.6) μ g/L, respectively. Out of 98 ground water samples of Jacobabad city, 16 samples were found above the permissible limits of WHO (~16.3% of total samples). Hence, water can be used for drinking purpose with carefulness.

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Introduction

Water is one of the most important and abundant compounds of the ecosystem. All living organisms on the earth need water for their survival and growth. As of now only earth is the planet having about 70% of water. On a global scale, groundwater represents the world's largest and most important source of fresh Potable water. Groundwater provides potable water to an estimated 1.5 billion people worldwide daily and has proved to be the most reliable resource for meeting rural water demand (Acharyya, S. K., 1999). But due to increased human population, industrialization, use of fertilizers in the agriculture and man-made activity it is highly polluted with different harmful contaminants. Therefore it is necessary that the quality of drinking water should be checked at regular time interval, because due to use of contaminated drinking water, human population suffers from varied of water borne diseases (Ahsan, S., 2009).

Generally the major sources of water pollution and ultimately of waterborne diseases are considered to be the direct discharge of domestic and industrial effluent wastes, leakage from water tanks and poor management of farm wastes (Jain et al., 2005). Various researchers have shown that drinking water in many countries does not meet WHO standards. Water pollution is one of the major threats to public health in Pakistan. Drinking water quality is poorly managed and monitored. It is deteriorating mainly as a result of disposal of the municipal and industrial wastewaters and also because of the saline drainage flow from agricultural areas (Signes-Pastor, A.J., 2009). Recent reports of UNICEF and WHO have revealed 748 million people around the world lacking access to safe water resources and over 2.5 billion people suffering shortage of water supply (Pradhan, R., 2003 et al). Since water is polluted and contaminated day by day due to anthropogenic activities, waste disposal mismanagement, industrial effluent and usage of pesticides Arsenic (As) is major concern for human health due to its presence in ground water that is used for drinking purpose (Hughes, MF. 2002). Mobilization of As in atmosphere has many factors such as natural ways like weathering of rocks, eruption of volcanoes and degradation of biological activities The man-made activities like combustion of fuel, coal, coke, using insecticides, herbicides, crop disinfectant medicine and other anthropogenic activates as smelting, mining and an additive usage of As to livestock feed for poultry as well as for wood preservative To the best of our knowledge no report has been published regarding the quality of water of Jacobabad city, Sindh, Pakistan. The purpose of this research was to evaluate the potential hazards of As in groundwater of different union councils of Jacobabad using flame atomic absorption spectrometer (FAAS) and to measure the health risks associated with As contamination (Kitchin, KT. 2001).

Water used for drinking purpose must be free from suspended particles, clear, odorless, and colorless contain pleasant taste with enough quantity of necessary minerals and that must be without any pollutant. Significance of drinking water possessions underutilization and its recycling requires too much quantitative organization and also a careful excellence examination by means of complicated equipments. Till now, no any detailed investigation using sophisticated instruments has been carried out for drinking water quality in Jacobabad District (under study area) by any government or national agency which may be trusted for its quality.

As a result, the arsenic investigation in ground water of this study area was very much necessary so as to aware the people of this region to combat the hidden enemy inside their drinking water. It is worth to mention here that the people of this area were suffering from strange and not curable diseases might be due to arsenic exposure. The aim of this study was to locate the actual concentration of arsenic in ground or public intake water of Jacobabad city and to distinguish the likely pollution sources with the help of statistical and geochemical data. The samples from many sites of Jacobabad city have been collected and analyzed for the arsenic hunt using hydride generator system coupled with atoimic absorption spectrophotometer.

However in Pakistan, more than 40% population bear the as contamination in water. Hence, nation of

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Pakistan has more risk exposure of As. More than 20% people living in Punjab are suffering from higher pollution of As in either ground or surface water sources but tolerate higher quantity of As in industrial areas. Although the aim of study was to determines the concentration of As in ground water which is main source of drink inking water source of local peoples. Also it was to ensure that whether the levels are exceeding or below the WHO proposed limits and also aware the responsible sectors to focus regarding water qualities of Jacobabad city.

Materials and methods

Study Area Description

Jacobabad or Khangarh is a district as well as Taluka the administrative center, belongs to province Sindh, Pakistan. The climate of Jacobabad is mostly hot and arid; area has very hot summers and mild winters. Higher and lower noted temperatures of area under study are; 127°F (52.8°C) and 25°F (-3.9°C) respectively. The rainfall is usually observed in monsoon season such as; from July to September (Nickson, R., 1998).





Sample Collection

It is always advised to get groundwater sampling by hand pumps 5 min in order to remove sand and insoluble impurities as well as depth water must be obtained to contain desired elemental quantities. Water was obtained from hand pumps having depth 80–100 feet. After running water, samples were attained. Plastic bottles were used to collect 1000mL water. Seven UCs of Jacobabad city were selected to acquire water samples of hand pumps and small motors used in houses to draw water from the ground with depth 80 to 120 feet as shown in Fig. 1. Method of collection of water samples from different points of Jacobabad was done with the help of global positioning system (GPS) in 2016-17. A total of 98 samples were obtained from all UCs of Jacobabad cities. Samples were shifted to laboratory to protect them from atmosphere and kept at room temperature to avoid their pH and temperature. Experimental work was carried out for checking of their chemical parameters in the laboratory.

Chemicals and reagents

Standard solution was prepared from reagents purchased from Merck (Darmstadt, Germany) and diluted with de-ionized water for required concentration of ppm solution for detection of As.

Instrumentation

This study was conducted using latest techniques of analysis such as Modern Atomic absorption

spectroscopic (Perklin A A100) coupled with Mercury Hydride System (MHS-15) to measure the contamination of As in water. This technique provides a simple and précised measurement of quantitative and qualitative analysis of metals present in different samples of water.

Microwave digestion method

500mL of water samples were put in PTFE flask, then flasks were closed and subjected to microwave irradiation in closed vessel microwave digestion system using Milestone Ethos D model (Sorisole-Bg, Italy). Digestion programmed of microwave oven was applied at 100W (2 min), at 250W (6 min), at 400W (5 min), at 550W (8 min) and ventilation for 8 min. The contents of the flasks were cooled and then diluted to 10mL with (0.2 M) HNO3. Similarly reagent blanks were also made by same procedure. Microwave digestion method has superiority to conventional digestion method because it takes less time to digest water sample as well as it has less chance of evaporation of elements so more accurate extraction of elements from samples than in conventional method. It also uses less acid for digestion (Rahman, A., 1996).

In total 98 samples of groundwater were collected from seven Union Councils of Jacobabad city during the year 2016-2017 followed by ISO sampling procedure 5667 method (ISO5667-3, 2012). The method cluster sampling was adopted for statistical significance. Coordinates were also noted with the help of Global Positioning System (GPS) for the authenticity of results. Before sampling hand pumps were run until fresh water at about 2-3 minutes. Polypropylene bottles of 1.5L capacity were used for collecting groundwater samples. To acidify samples; 1mL of concentrated HNO3 was added. Samples were immediately transported to the research laboratory Institute of Chemistry, Shah Abdul Latif University Khairpur after collection. However; prior to analysis samples were preserved at 4°C.

Sample Preparation

For arsenic determination from ground water; 98 samples collected from seven Union Councils were

prepared according to the method give below; 1L capacity beakers were used for sample evaporation in which 500mL water sample was taken and samples were heated at the temperature of 80 to 90°C by using electric hot plates. Volumetric flasks of 25mL capacity were used to store the evaporated samples. Samples were filtered by Whatmann #42 filter paper and volume was made up to the mark with de-ionized water. Concentrated HNO₃ was used for preserving the samples. Samples were analyzed by using highly sensitive machine of AAS coupled with mercury hydride generator (HG-AAS) for the determination of arsenic concentration.

Water Analysis

Arsenic was analyzed from collected water samples by using Atomic Absorption Spectroscopy (AAS) Perkin Elmer AAS-100 Analyst. AAS was coupled to hydride generation system (HG-AAS) fallowed by USEAP method (USEPA, 2010). Calibration of instrument was carried out by using arsenic standards of 1.0µgL⁻¹ to 10µg^{L-1} and dilution of samples was performed by using doubled distilled water. To get rid of organic contaminants present in plastic bottles; washing with 10% nitric acid solution was carried out before sampling. After that de-ionized water was used for washing purposes three times and labeled properly. Sketch of area, global positioning system (GPS) and time were also recorded.

Analytical Procedure for Arsenic using HG-AAS Method

For arsenic analysis; standard solution of different concentration range were used to calibrate the AAS machine coupled with hydride generation system. Standard solutions were prepared by using 1.5% HCl solution. For getting arsine gas; 63% sodium borohydride and 10% potassium iodide solutions were added. For moving sample and standard into preheated atomizer; argon gas was used. Blank analysis was followed by standard analysis throughout the entire process. From calibration graphs; amount of arsenic was measured. All experiments were performed at room temperature followed by familiar laboratory protocols. Acidic blank through sample inlet was used for 5 to 10 minutes to increase the HG-AAS method (Smith, A. H., *et.al*)

Results and discussion

Table 1. Arsenic $(\mu g/L)$ level in ground water of different UCs of Jacobabad city.

Sample No:	UC-1	UC-2	UC-3	UC-4	UC-5	UC-6	UC-7
1	15.0	08.0	05.0	04.0	05.0	05.0	04.0
2	08.0	08.0	06.0	11.0	04.0	08.0	10.0
3	05.0	05.05	15.0	10.0	10.0	11.0	13.0
4	08.0	05.0	07.0	05.0	8.00	16.0	08.0
5	05.0	08.0	08.0	07.0	12.0	11.0	05.0
6	10.0	08.0	10.0	13.0	05.0	22.0	09.0
7	15.0	12.0	07.0	06.0	07.0	07.0	04.0
8	06.0	11.0	04.0	07.0	10.0	10.0	10.0
9	08.0	05.0	05.0	08.0	05.0	10.0	03.0
10	05.0	08.0	09.0	01.0	11.0	05.0	09.0
11	06.0	06.0	08.0	05.0	07.0	11.0	07.0
12	09.0	09.0	08.0	05.0	10.0	08.0	07.0
13	07.0	05.0	08.0	08.0	05.0	15.0	12.0
14	09.0	05.0	03.0	05.0	08.0	03.0	10.0
Mean	8.29	7.36	7.36	6.79	7.64	10.15	7.93
Standard deviation	3.27	2.30	2.95	3.09	2.62	4.99	3.08

Table 1. Shows comparative mean values of As level in ground water of total seven Union Councils of Jacobabad city. From each union council 14 sampling station were chosen for ground water analysis and the mean value of each union council was also recorded. In UC-1 two sampling spots recorded as highest As levels $(15(\mu g/L))$ and rest of them were below that levels. For more analytical accuracy the Standard deviation was also calculated of each union council. By comparing all investigated UCs it was found that the highest level was found in UC-06 as mean concentration of As level in ground water ($10.15\mu g/L$). Remaining UCs were noted below that mean level and lowest level was found in UC-04 as (4.99µg/L). Besides this all Union councils of Jacobabad city has As values in ground water that were found within safe limit of WHO recommended values.

Through these findings local peoples who were routinely consuming this pollutant growing water will much aware regarding the poor quality of ground water. In Jacobabad city there is lack of water treatment plants and people are totally dependent to consume poor ground water through hand pumps and tube well. But many cities of Sindh have still uncovered and suffering from poor quality of ground water. So for we had investigated a major part of investigated area to alarm the different government and other public food and water quality agencies to focus on rising level of As in ground water.

Table 2. Arsenic daily intakes from drinking water of different UCs of Jacobabad city.

UCs No:	UC-1	UC-2	UC-3	UC-4	UC-5	UC-6	UC-7
As Mean	8.29	7.36	7.36	6.79	7.64	10.15	7.93
ADI	0.44	0.39	0.39	0.36	0.41	0.54	0.42
Notes: Safe As daily intake in water 0.66µg/day. As							
(µg/L)).						

Total arsenic daily intake was observed of all union councils which is mentioned in Table: 2.In UC -o6 the highest ADI was recorded as (0.54µg/day). The second highest ADI level of As was noted as (0.44µg/day) in UC-1 and UC-7 has (0.42µg/day) recorded to be the third highest ADI level from study area. UC-06. The minimum ADI level was observed in UC-04 as (0.36µg/day). Although it was observed that As accumulation in body was found within safe limit as proposed by WHO and other food regulatory authorities. The daily water intake and body weight of common people were assumed average (3.0µg/day) to (3.5µg/day) liters and 65 kg, respectively. However these findings shos the growing level of Arsenic daily intake within the consumer's body, so responsible authorities should take some serious step to eradicate or stop growing level of Arsenic in mentioned study area.

Table 3. Concentration on As in different cities ofSindh and Punjab Provinces.

	-		
Province	City	As $(\mu g/L)$	References
Punjab	Shiekhupura, Multan	2-900	Nusrat Ehsan <i>et al.,</i> 2018
Sindh	Jacobabad,	0.01-17	
	Khairpur,	0.04-30	Abdul Hameed
	Thatta,	0.01-29	Kori <i>et al.,</i> 2018
	Hydarabad	0.01-300	

Table 3 Determines As contamination of ground water quality of various cities of Sindh province including Jacobabad city, which determines that studied area ground water has lowest values among compared cities of Sindh as well Punjab province. Many studies have reported high concentration of As in different cities such as in Nawab Shah, As concentrations in the ground water ranged at 10–

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 200μ g/L. These values were too high to bear the burden of contaminants for local population. In upper part of Dadu, ground water quality was found polluted with As contamination. The level of As in the water of Dadu was reported in the range of $8-67\mu$ g/L. The study concluded that 10% of ground water samples were exceeded the limit of WHO permissible level and found unsafe for drinking purpose.

Word wide comparison of As concentration in ground water determines the concentration of As in ground water of Jacobabad city has much lower level $10\mu g/L$ to $17\mu g/L$ in some UCs. But it can be deteriorated with passage of time as neighboring countries of Pakistan such as India and Bangladesh where people are suffering from too much contamination of As $2000\mu g/L$ and $4104\mu g/L$ respectively in ground water.

Table 4. Pearson correlation of Arsenicconcentration of different UCs of Jacobabad city.

Name of UCs	UC-01 UC-02	UC-03	UC-04	UC-05	UC-06	UC- 07
UC-01	1.000					
UC-02	1.000**1.000					
UC-03	-0.135 -0.135	1.000				
UC-04	-0.128 -0.128	0.284	1.000			
UC-05	0.137 0.137	0.244	-0.437	1.000		
UC-06	-0.145 -0.145	0.409	$.627^{*}$	-0.240	1.000	
UC-07	-0.316 -0.316	0.396	0.318	0.163	0.205	1.000
Notoe	*Correlation	, ic c	ignificor	nt at t	ha or	lovol

Notes: *Correlation is significant at the .05 level. **Correlation is significant at the .01 level.

Table 5 shows Pearson correlation of studied UCs of Jacobabad city. It was observed that UC-1 showed strong relation with UC-4, 6 and 7, less strong relation with UC-7 and weak relation with UC-2, while negative relation was detected with UC-3, 5, 6 and 7. UC-2 indicated strong relation with UC-5 and significant relation with UC-3, 4, 6 and 7. It showed negative relation with UC-5, 6 and 7. In UC-3, it was noticed less strong relation with UC-4, 6 and negative relation with UC-5, and 7 while weak significant relation with UC-4, 6 and negative relation result showed contamination of ground water with As was man-made activities, erosion of bed rocks, homes, industrial effluent, agricultural runoff activities and solid waste dumping.

Conclusion

Maximum number of samples of UC-6 was observed contaminated due to the presence of higher level of arsenic as compared to other UCs of Jacobabad city. The lowest number of samples was found contaminated in UC-3; whereas similar trend of % contamination of arsenic was observed in UC-1, UC-2, UC-5 and UC-7 in study area. Health assessment revealed that maximum number of people were infected possibly due to arsenic in groundwater belonged to UC-6 and UC-4; while less number of persons were found affected because of lower level of arsenic contamination in UC-3 of Jacobabad city.

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