Contamination of Arsenic in Public Water Supply Schemes of Larkana and Mirpurkhas Districts of Sind

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(Received 8th November, 2005, revised 24th January, 2006)

Summary: Arsenic (As) contamination of drinking water is now a global issue and is present all over the world. In response to the growing concerns about this poisonous carcinogen and awareness of the dangers of As in drinking water, an exclusive study was carried out on the occurrence and distribution of arsenic in drinking water samples, collected from ten (10) villages of District Larkana, and seven (07) villages of District Mirpurkhas, in Sind province. The samples were collected from different public water supply schemes, where the drinking water quality is known to have been deteriorated. In all the study areas of Mirpurkhas, arsenic concentration was found below the maximum permissible limit as recommended by World Health Organization (WHO). An average concentration of 2.04 ppb was observed in water samples of Mirpurkhas with a narrow variation, however in Larkana District, concentration of arsenic was found in samples with a lot of variations in the range of 0.40-20.02 ppb. Altogether 10% of the water samples of District Larkana exceeded the WHO guideline of 10ppb. As compared to Mirpurkhas, District Larkana has appeared as a more problematic zone from the point of view of arsenic contamination in the particular study area.

Introduction

Subsequent upon growing public concerns over the deteriorating water quality, more recently the behavioral role of trace metals has been studied in great depth [1, 2]. Extensive studies have been undertaken by various workers to characterize water pollution in terms of the presence of various trace metals in natural surface and ground water [3, 4]. Even a few years back the contamination of water by arsenic was not so common, and it has come into prominence due to the increase in ground water consumption and use of tube wells for drinking water. However now a days several ailments are quite prevalent and known to be caused by arsenic [5, 6].

Arsenic, an ubiquitous element that ranks 20th in abundance in the earth crust, 14th in seawater and 12th in human body [7] has both natural and anthropogenic sources. The average concentration of arsenic in the earth crust is about two parts per million by weight, however its concentration in the rocks and soils are highly variable [8]. Since its isolation in 1250 AD by Albertus Magnus, this element has been a centre of controversy in human history [9] as arsenic is four times as poisonous as mercury. Arsenic naturally occurs in two forms, which are organic and inorganic arsenic. Toxicological studies indicate that organic arsenic is of lower toxicity than inorganic arsenic. In general it is found that organic arsenicals are more rapidly excreted than inorganic forms and pentavalent arsenicals are cleared faster than trivalent [10]. Routes of arsenic intake in vivo considered are respiratory for dust and fumes, and oral for arsenic in water, beverages, soil and food. Few investigations of dermal absorption rates for arsenicals are undertaken [11]. In drinking water arsenic is found as inorganic and therefore this poses a great hazard to human health. Clinical manifestations of arsenic poisoning begin with various forms of cancers including skin, bladder, lung, kidney, liver and prostrate, as well as cardiovascular and neurological effects have been also attributed to inorganic arsenic.

Regular use of arsenic polluted water, over long period of time, can cause an unacceptably high concentration in the human body, leading to the onset of various diseases. The contamination of water from arsenic and its health impact on humans have already been reported from 23 regions in different parts of the world. The magnitude of this problem is severe in Bangladesh followed by West Bengal, India [12] and China [13]. In recent years evidence of arsenic

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contaminating water has also emerged in other Asian countries including: Lao PDR, Combodia, Mayanmar and Pakistan [14].

Sind, the 2nd largest province of Pakistan by population and its adjoining region cover an area of about 70,000sq. miles and classified as a thickly populated region of Pakistan [15]. Due to arid and semi-arid climate, the water resources are not only insufficient, but due to poor management of the available water, the quality of drinking water is gradually deteriorating day by day.

Taken together with the discovery of arsenic in ground water in other countries, it was thought necessary that drinking water of concerned areas should be tested for arsenic, because characterizing regional variations in ground water chemistry is essential for identifying impaired and pristine ground water by monitoring long term trends in ground water. The reduction of the WHO provisional guideline value for As concentration in drinking water from 50 ppb to provisional 10 ppb in 1993 [16], and the reduction in 2002 of the USEPA Maximum Admissible Concentration (MAC) to 10 ppb, has been made in response to growing concern about this poisonous carcinogen and has raised awareness of the dangers of As in drinking water. In view of the health concerns outlined above, and alerted by the magnitude of the problem afflicting nearby Bangaldesh and West Bengal, PCSIR Labs Complex Karachi has undertaken a survey of arsenic concentration in drinking water of Larkana and Mirpurkhas Districts of the province Sind.

Results and Discussion

The chemical assessment of the water samples, collected from public water supply schemes located in main districts of Sind province, like Husri Hyderabad, Sakrand, Ghotki, Mirpurkhas, Larkana, & Badin, was carried out for pH, alkalinity, electrical conductance, hardness, Sulfate, Chloride, Sodium and Potassium in order to have a baseline data and an idea about the type and quality of water in these regions. The results in Table-1 show that most of the water samples have dissolved minerals beyond the levels of the WHO recommended guidelines & therefore are chemically unfit for human consumption .Mostly the water samples of this particular area are of sodium-chloride type, which is saline in nature and therefore indicating the deposition of minerals in corresponding aquifer system.

Natural enrichment of water by As may arise in several ways [17], viz. hydrothermal volcanism, oxidation of arsenical sulphide minerals, reduction of Fe OOH and release of its sorbed load to ground water desorption of As from mineral sorption sites in response to increase of pH and evaporation concentration [18].

Studies have shown that the saline environment generally supports the uptake and excretion of trace and toxic metals from their corresponding minerals [19-20] and arsenic is one of them. The results of analysis obtained in drinking water samples, collected from different villages of the two main districts of Sindh, through different public water supply schemes, with particular reference to arsenic, have been discussed separately.

Arsenic Distribution in Mirpurkhas:

The average quality of water in District Mirpurkhas is deteriorating and is brakish in nature (Table-1). The concentration of all the major ions has been found beyond the maximum permissible limit (MPL) of WHO, and is therefore not fit for human consumption.

Table-4 gives the overview of the average concentration of arsenic in water samples collected

Table-1: Analysis of Water Samples Collected From Main Districts of Sind

S. No.	Parameters	Husri (Hyderabad)	Sakrand	Ghotki	Mirpurkhas	Larkana	Noshehro Feroze	Badin	WHO guideline
1	pH	6.93	7.92	7.68	6.98	8.05	7.48	7.30	6.5-8.5
2	Calcium (ppm)	210	104	58	800	10	72	184	-
3	Magnesium (ppm)	68	71	32	825	10	40	90	-
4	Sodium (ppm)	301	310	62	3300	265	135	850	200 ppm
5	Potassium (ppm)	2	13	1.5	9	0.9	1.4	5	-
6	Chloride (ppm)	404	226	140	5775	94	47	754	250 ppm
7	Sulfate (ppm)	436	536	138	3910	260	122	1244	250 ppm
8	Bicarbonate (ppm)	506	418	268	387	283	447	357	-
9	Alkalinity as $CaCO_3$ (ppm)	415	343	220	317	232	367	293	-
10	Total Dissolved Solids (ppm)	1846	1546	552	16330	830	672	3456	1000 ppm

Fig. 1:

Table-2: Existing Standards of Arsenic in Drinking Water

S. No.	International Standards	Maximum Allowable Limit
1	World Health Organization (WHO)	10 ppb
2	US Environmental Protection Agency (USEPA)	10 ppb
3	Bangladesh Standard (BSTI)	50 ppb
4	Pakistan Standard Quality Control Authority (PSQCA)	10 ppb
5	Indian Standard	50 ppb

Table-3: Arsenic Bearing Minerals

S. No.	Minerals	Chemical Formula
1	Arsenopyrite	Fe As S
2	Realgar	As S
3	Orpiment	$As_2 S_3$
4	Enargite	$Cu_3 As S_4$
5	Tennantite	$Cu_{12} As_4 S_{13}$

from seven villages. The mean concentration of arsenic in water samples collected from Mirpur Khas District was found to be 2.04 ppb and ranged between 0.58-4.64 ppb. It may further be seen in Table-4, that in all the water samples, collected in triplicate, arsenic have been found below the existing

Table-4: Distribution of Arsenic in various locations of District Mirpurkhas

S. No.	Location	Arsenic Mean ± S.D (ppb)	RSD %
1	*W/S scheme Gul Lashari	3.72 ± 0.002	0.2956
2	W/S scheme Abdul Haq and Adj Village	3.10 ± 0.002	0.0645
3	W/S scheme Gul Muhammad Palli	4.64 ± 0.002	0.0431
4	W/S scheme Har Palli and Adj Village	1.16 ± 0.001	0.0862
5	W/S Scheme Abdul Hakeem and Adj Village	1.54 ± 0.001	0.0649
6	W/S scheme Khalarai and Adj Villages	3.28 ± 0.002	0.0609
7	W/S scheme Mirpur Khas	0.58 ± 0.0005	0.0862

*W/S = Water Supply

Table-5: Distribution of Arsenic in various locations of District Larkana

S. No.	Location	Arsenic Mean ± S.D (ppb)	RSD %
1	*R/W/S scheme Bhuthi Lashkas Khan	1.06 ±0.006	0.5660
2	R/W/S Scheme Panhwaro Sono Waggan	2.78 ±0.008	0.2877
3	R/W/S Scheme Kandhi	0.40 ±0.004	1.000
4	R/W/S Scheme Karramullah	**BDL	-
5	R/W/S Scheme Mirpur Sakhani	BDL	-
6	R/W/S Scheme Jahan Khan Marfani	20.02 ±0.024	0.1198
7	R/W/S Scheme Duri Mashi	2.860 ± 0.008	0.2797
8	R/W/S Scheme Sawai Chandio	0.58 ± 0.009	1.5517
9	R/W/S Scheme Karohar	1.74 ± 0.008	0.4597
10	R/W/S Scheme Meenhal Shabrani	6.40 ± 0.016	0.25

* R/W/S = River Water Supply
**DDL = Below Detection Limit (0.2 ppb)

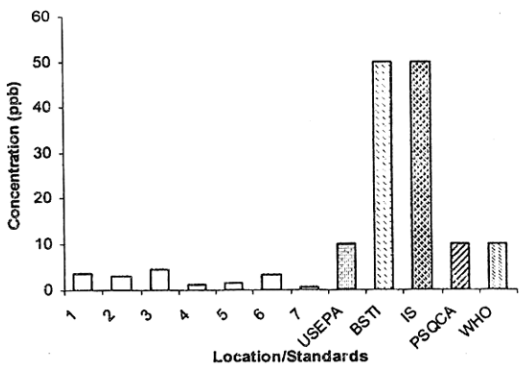

Fig. 2: Comparative overview of As Distribution with existing standards in Mirpurkhas.

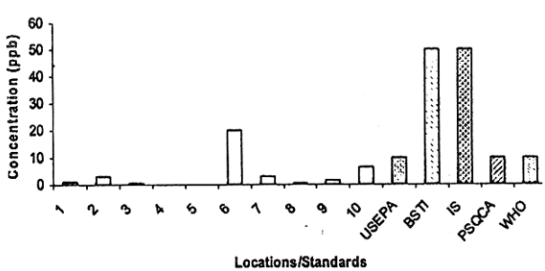

Fig. 3: Comparative overview of As Distribution with existing standards in Larkana.

limit of different international standards like WHO, PSQCA, BSTI,USEPA and Indian Standard [12, 21, 22], (Table-2). The minimum concentration of 0.58 ppb was observed in the samples collected from water supply scheme of Mirpur Khas while that of maximum (4.64 ppb) was found in Gul Mohammad Palli and adjoining villages. However the overall picture, as regards arsenic concentration in water samples of Mirpurkhas District, is not satisfactory, as long exposure of arsenic up to this level, might create many physiological disorders in local consumers of this essential commodity.

Arsenic Distribution in Larkana District

Larkana is another big division of Sind with thick population. From this area of study, three (03) water samples were collected from each of the village. Table-5 shows the pattern of average arsenic concentration in water samples through various public supply schemes, collected from ten different villages.

In Karamullah and Mirpur Sakhani villages, arsenic was found to be below the detection limit. Occurrence of arsenic is very sporadic and marked differences in concentration occur even at very short distances, sometimes even less than 2 to 3 km. The mean arsenic concentration in the particular District, was found to be 3.58 ppb within the wide range of 0.40 - 20.02 ppb. The minimum concentration of 0.40ppb was found in scheme of Kandhi, while maximum of 20.02 ppb was analyzed in water sample, collected from the scheme of Jahankhan Marfani. It may further be seen in Table-2, that the concentration of arsenic in about 10 to 20% water samples from Larkana district have been found to exceed from the maximum permissible limit recommended by WHO, USEPA and PSQCA, but still below to the Bangladesh (BSTI) and Indian Standard, as shown in Table-2.

The presence or absence of dissolved arsenic is a reliable surrogate indicator of reduction-oxidation conditions in a local aquifer and/or well. Climate and geology play an important role in determining the amount of arsenic in water systems. The most prominent source of arsenic in ground water begins with the oxidation of sulfide minerals mostly occurring in sedimentary rocks (Table-3). Current hypothesis suggests that the iron-oxides are formed by the oxidation of arsenopyrite and arsenic

is incorporated in these hydroxides, particularly in alluvial environmental conditions [8].

The geological factors that determine the distribution of arsenic in water samples, collected from both the districts are poorly understood. It is known that arsenic is a naturally occurring chemical element in rock and soil, and is present in trace amounts in ground water and therefore its presence in ground water is largely the result of minerals dissolving naturally over times as rocks and soil weather [23]. Many main sources of arsenic in the environment include mining and smelting operation, agricultural applications and the use of industrial products and disposal of wastes containing arsenic. Large arsenic doses above 60 ppm may cause death, while lower dose (10 - 30 ppm) causes stomach and intestinal irritation and nervous system disorders [24].

A collaborative effort, by PCRWR and UNICEF in the year 2000 through field testing of ground water in all the four provinces of Pakistan was initiated. According to the study in Sind province, it has been found that, 36 % and 16 % of population was exposed to arsenic contaminated water over 10 ppb and 50 ppb respectively. The districts with quite higher concentration of arsenic in groundwater, were Dadu, Khairpur, Nawabshah and Tharparkar [25]. The situation in Mirpurkhas and Larkana is not as alarming as in the above mentioned districts. Maximum arsenic was found to be 20.02 ppb in Scheme Jahan Khan Marfani, District Larkana.

Arsenic, in drinking water is of major concern to many of the water utilities in the world. Numerous studies have examined the removal of arsenic from drinking water through treatment processes such as coagulation precipitation, reverse osmosis and ion – exchange etc. Although arsenic status, in both the districts being studied, is not alarming at the momentum, but necessary preventive measures should be adopted for further aggravation in this respect.

Experimental

Sample collection and chemical analysis

Polyethylene screw-capped bottles (1.5 litre capacity) were used to collect the samples, prior to use, sequentially cleaned with the detergent, washed several times with tap water, soaked for 24 hours in 1%HNO_3, again rinsed with tap water, several times rinsed with distilled water, dried at 100 ^{0}C for 1 h and finally cooled at room temperature, capped and labeled. All necessary measures were taken while filling up the samples and during their transport and storage.

All the reagents used, were of analytical grade and standard analytical methods were followed for the assessment of normal drinking water parameters like Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and SO_4^{2-}. The analysis was carried out in triplicate to get the reliable data and mean values were recorded for each parameter. pH, temperature and electrical conductance were measured immediately, after collection of samples, using portable digital pH Meter and conductivity meter JENWAY /E.U/430 pH/cad./ portable/02162. All other estimations were finished within 48 hours of sampling.

Analysis of sulfate and total dissolved solids were carried out by gravimetry, chloride by argentometric titration method, calcium and magnesium by complexometry, whereas alkalinity was determined by HCl titration. Sodium and potassium were determined by Flame Photometer, FES Corning 410 [26].

Arsenic analysis

For the determination of Arsenic, a Hitachi Z-5000 Spectrophotometer equipped with a single element hollow cathode lamp, Zeeman background corrector and ZAA software for electronic processing of the results, coupled with hydride formation system was used. For the acid channel 1.2 N HCl and for the reducing channel $NaBH_4$ (1%) in NaOH (0.4%) was used. The samples were treated with 20 % KI in order to reduce all the arsenic 'V' to arsenic 'III'. Blank and samples were also treated in the same manner. The calibration curve was obtained using standard solutions at respective concentration of 1, 2, 3, 4 and 5 ppb, prepared from stock solution of 1000 ppm, Merck.

Conclusions

Samples of drinking water of District Larkana have found to be posing more danger, as in some samples concentration of arsenic was found to be higher than the maximum allowable limits, recommended by WHO and USEPA .Further their

chemical analysis does not suggest their suitability for human consumption. As the impact of arsenic extends from immediate health effect to extensive social and economic hardship, therefore its eventual impact on the lower strata of the population needs special attention and demands long term strategical measures to combat this potent threat.

References

1. W. H. Hatting, Water S. A, **3**, 104 (1977).
2. V. Ekrem Kalmaz, *J.Environ Science*, 23-24, (1980).
3. T. H. Sibley and J. J Morgam, *Proc Int. Conf Heavy Met. Environment Toronto*, 1, 319 (1975).
4. W. Stumm and H. Bilinski, Proc 61st Int conf, New York (Pergamon Press), pp.39 (1972).
5. A. A Khan and M. K. Ahmed "Is Arsenic contamination in our Ground water ?" Daily Star, 2nd July (1995).
6. A. H. Smith, E. O. Lingas and M. Rahman, *Bull. of World Health Organization*, **78**, 1093 (2000).
7. J. E. Spance, *Arsenic in Ground Water*, **30** (3), Fall (2000).
8. R. J. Sullivan, National Air Pollution Control Administration Publication No. APTD 69-26, Raleigh, NC. P.60, (1969).
9. U. S. Environmental Protection Agency, Interim Primary Drinking Water Standards, Fed. Reg. 40 11, 990 (1975).
10. WHO Arsenic Compounds, Environmental Health Criteria. 2nd ed. World Health Organization, Geneva, (2001).
11. M. M. Rehman, M. K. Sengupla, S. Ahmed, U.K, Choudhery, Md. A Hussain. B. Pas, D. Jodh, K. C. Saha, S. Pati, I. Kaics, A. K. Barua and P. Chakrasorti, *Sci. of the Total Env.*, 338. 189 (2005).
12. M. M. Rehman, B. K. Mandal, R. T. Chowdhry *J. Environ. Sci. Health*; **A 38** (1); 25 (2003).
13. Y. Xia, J. Liu, *Toxicology*, **198** (1-3), 25 (2004).
14. ESCAP-UNICEF-WHO Expert Group Meeting DV. Economic and Social Commission for Asia and the Pacific; Bangkok; May 2-4, (2001).
15. F. E. Eames, *Geol Mag*, **87**, 214 (1950).
16. WHO Guidelines for Drinking Water Quality, 2nd ed., 1, Recommendations Addendum, Geneva, Switzerland (1993).
17. A. H. Welch, D. B. Westjohn, D. R. Helsel, R. B. Wanty, *Ground Water*, **38**, 589 (2000).
18. R. T. Nickson, J.M. McArtur, B. Shrestha,T.O. Kyaw-Myint and D. Lowry, *Applied Geochemistry*, **20**, 55 (2005).
19. G. W. Bryan, *J. Mar Biol, Assoc (UK)* **53**, 145, (1973).
20. M. Jamaluddin Ahmed, *Pak. J. Anal. Chem,*. **4**(2), 133 (2003).
21. PSQCA , 4639-2002, 1st Rev.
22. Arsenic and Ground water, USGS-Chehalis River Council May (2000).
23. Find Rule, National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring, Federal Register (FR), 66 (14), 6976-7066,22nd January, (2001).
24. E. A. Wolson, *ACS Ser.*, 7, 1, (1975).
25. T. Ahmad. M. A. Kahlown, A. Tahir and H. Rashid, 30th WEDC International Conference, Vietnam, Lao PDR, 459 (2004).
26. Standard Methods for the Examination of Water and Waste Water, 20th Ed. APHA, (1998).