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Arsenic exposure assessment from ground water sources in Peshawar Basin of Khyber Pakhtunkhwa, Pakistan

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Abstract

Arsenic contaminated groundwater in some south Asian countries like Bangladesh and West Bengal India is one of the largest environmental health hazards in the world. PCRWR with the help of UNICEF has carried out a nationwide survey for drinking water arsenic contamination in different parts of Pakistan which also included limited number of samples from Mardan, Peshawar and Mingora in KPK province. In order to know the existence of arsenic contamination in ground water of the Peshawar basin, about 30 drinking exposure (human hair and nails samples from different parts of the Peshawar basin have been collected. Drinking/cooking water, raw rice, hair and nails samples were analyzed for total arsenic by ICP-MS. Chronic Daily Intake (CDI mg/Kg Body weight) was calculated for arsenic risk assessment of all the volunteers who participated in this study. All drinking/cooking water samples were found below the 10 µg/L arsenic concentration which is the WHO provisional guideline values. The results were also confirmed by the biomarkers of arsenic exposure from the study population.

1. Introduction

Ground water arsenic hazard is world wide recognized problem which is reported in various parts of the world (Nickson, 1998; Polya, 2008; 2010; Rahman, 1996; Rahman, 2009; Sengupta, 2003; Smedley, 2002).

Different environmental exposures, for example drinking, cooking with arsenic contaminated water or eating arsenic contaminated food for example rice and other rice products and also the cooking methods of food are mainly responsible for arsenic contamination (Carbonell et al., 2009; Chakraborti et al., 2009a).

The health hazards (both carcinogenic and noncarcinogenic) associated with chronic intake of arsenic due to drinking arsenic contaminated water have been investigated and well known (Nickson, 1998; Acharyya, 1999; Ahsan, 2009; Argos, 2010; Shrestha, 2003; Smith, 2009; 1998). Because of its bioaccumulative nature and persistency in human (Huang, 2009; Hughes, 2006) USEPA declared inorganic arsenic as carcinogenic in nature.

Ground water arsenic problem is newly identified in Pakistan as a result of a national level survey program. At some places in Punjab and Sind provinces it is well above the maximum permissible limit of WHO (10µg/L) (Ahmad, 2004; PCRWR, 2003a, 2004; Arain, 2007; 2009; Farooqi, 2003; 2007; 2009; Nickson, 2005).

The maximum reported level of arsenic in ground water from Kalalanwala, Punjab province is about 1900 µg/L (Farooqi et al., 2007a) and 906 µg/L in Muzaffar Ghar district (Nickson et al., 2005). On the other hand up to 352 µg/L of inorganic arsenic in ground water (n=240) has been reported recently in Sind province (Baig et al., 2010) with a maximum of 250 µg/L from southern parts of Sind (Arain et al., 2007, 2009).

According to a survey of PCRWR (2002-2008) the major identified problems of drinking water are due to arsenic, fluoride, nitrates and bacterial contamination which needs to be addressed immediately (Farooqi et al., 2003, 2007b, 2009; PCRWR, 2008a).

In order to have an idea about the ground water arsenic situation in KPK province, five districts were selected and random sampling strategy was applied in this study.

2. Peshawar basin

The Peshawar basin is an intra-mountain basin (>5500 km^2) situated at the southern margin of the Himalayas and northwest of the Indus plain between the longitude 71° 15' and 72° 45' E and latitude 33° 45' and 34° 30' N in the North West Frontier Province (NWFP) (currently known as

KPK) of Pakistan. It is bounded by the mountain ranges of Khyber in the west and northwest, Attock Cherat in the south and Swat in the north and northeast while the Indus River borders its south eastern side where it is open for discharge of water. The west east flowing river Kabul and its tributaries irrigate the basin and join the Indus at eastern exit (Fig.1) (Tariq, 2001).

The Peshawar basin is fairly flat with average elevation of 300 m above mean sea level. The central part of the basin is generally covered with fluvial micaceous sand, gravels and lacustrine deposits while quaternary flanglomerates are lying along the margins of the basin. On the basis of varying lithologies, the quaternary sediments, covered soils and hosting aquifers of the Peshawar basin are classified as Peshawar piedmont, Peshawar floodplain and Peshawar lacustrine sediments, soils and aquifers respectively.

Both surface water and ground water irrigation is practiced in Peshawar basin. A number of dug wells are used for irrigation in Mardan and Charsadda areas. Irrigation department operated about 190 tub wells within Peshawar basin. These tube wells are used for irrigation purposes. Domestic water supply is served by the 609 wells drilled and operated by Public Health Engineering Department (PHED) whereas in rural areas there are also domestic wells in most of the houses (WAPDA 1994). There are four main rivers draining the Peshawar basin that is the Kabul River, the Swat River, the Bara river and the Kalpani Nala. Besides these rivers there are several perennial and non-perennial Nala that contribute to the Peshawar basin drainage system and ultimately discharge into the Kabul river. The Kabul River is the main river which drains almost the whole basin and enters the plain near Warsak and falls in the Indus River near Jehangira.

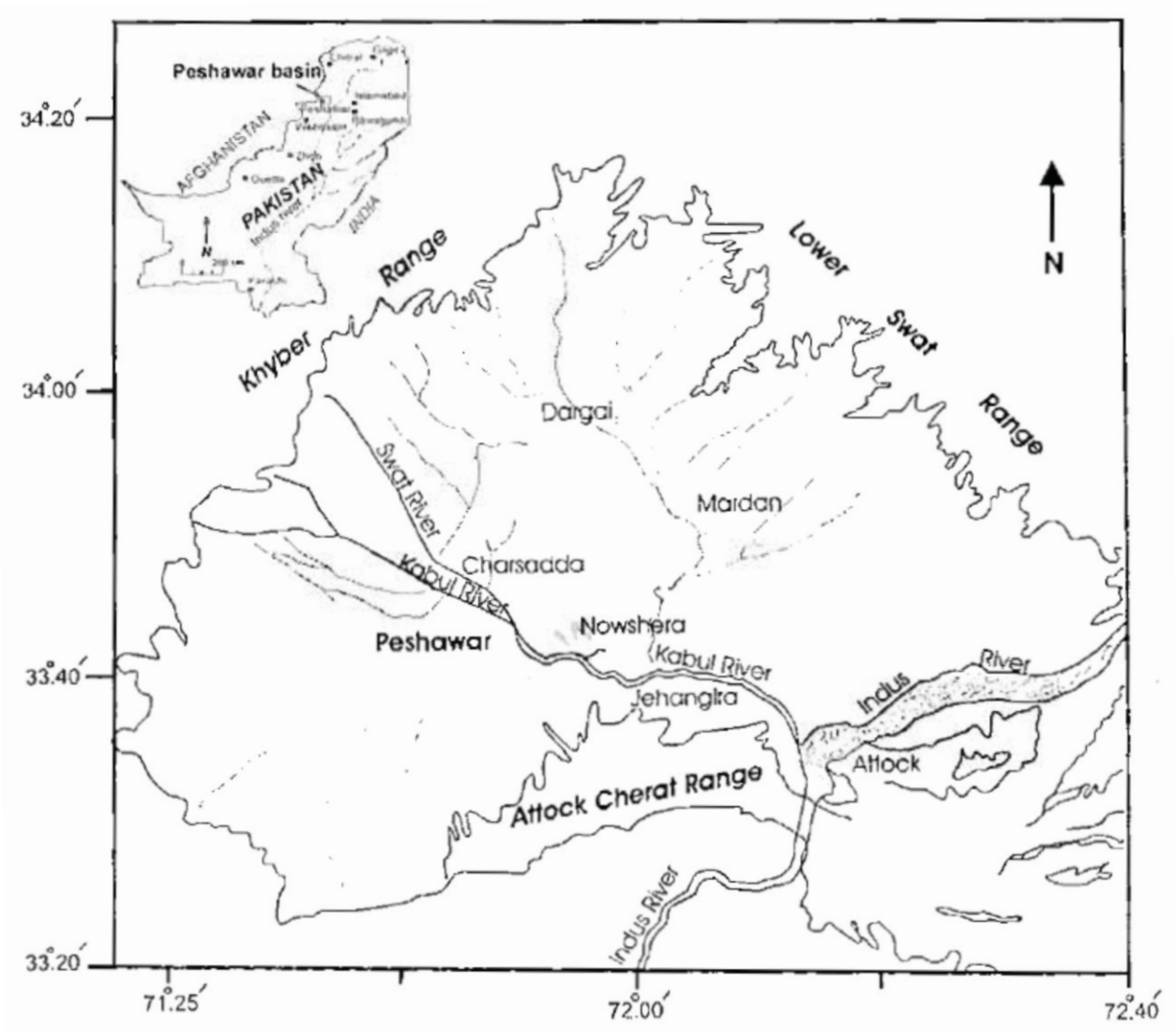

Fig. 1. Map of Peshawar Basin (including Peshawar, Mardan, Nowshera, Charsadda and Swabi) and the drainage system (After Tahirkheli & Burbank, 1985).

3. Climatic condition

The climate of the area ranges from semiarid subtropical continental lowland type in the western parts to sub humid to subtropical continental lowland type in the eastern parts of the basin. The rain fall ranges from 340 mm to 630 mm. The hottest months are June and July with an average daily temperature of 40-48 °C. January is the coldest month with an average daily temperature of -2° C. The mean annual potential evaporation is approximately 1200 mm in Mardan and Nowshera, 1100 mm in Charsadda and 1500 mm in Peshawar (WAPDA , 1994).

4. Population of the field Area

The Peshawar district has a population of 1,650,941 with a growth rate of 4.1%/annum (Population Census, 1999). The selected districts are the highly populated areas of KPK with the population density ranges from 500-1000 persons per sq. kilometer.

5. Methodology

5.1. Sampling and field survey

All the procedures of the study were ethically approved by the Ethics Committee of NCEG, University of Peshawar prior to the commencement of the study.

An informed consent based questionnaire survey was performed along with the sample collection in the field and a GPS was used for recording the exact sample location. Samples of ground water used for drinking as well as cooking purpose were collected along with hair and nail samples from volunteers. The samples were collected and analyzed by using standard methods of analyses accompanied by strict quality control measures. Some physical parameters were measured in the field while the chemical analysis was performed on ICP MS and ICP AES in the Williamson Research Centre of the School of Earth Atmospheric and Environmental Sciences, University of Manchester, UK.

The water, hair and nail samples were collected. Stratified random sampling method for the evaluation of different subgroups of population subjected to arsenic exposure for the risk assessment process have been applied as it has less subjectivity and more representativeness of the sample without increasing the cost and arsenic probability. Samples (n= 30) were collected from five districts (Peshawar, Mardan, Nowshera, Charsadda and Swabi) of Peshawar basin areas including urban as well as rural residents (Fig. 2). These samples were taken from both males and females including different age groups (12-75 years).

5.2. Questionnaire survey

Each participant was interviewed to complete a questionnaire, which asked for demographic, diet and information on potential exposure sources, such as source of drinking water, water consumption patterns, smoking patterns and about their present health status and any health problem especially skin problems, such as keratosis and melanosis.

5.3. Sample collection

Drinking water samples (unfiltered) were collected in acid-washed 500-mL polyethylene bottles from the kitchen tap, tube well (or other designated drinking water source, excluding bottled water). Precautions were made before taking the samples by allowing the water to run through the pipes for a maximum time of 5 minutes in order to purge the source. A labelled clean plastic bottle was filled to the top, and the lid replaced. Replicates samples were also collected. The water samples were transported to the geochemistry laboratory of NCEG, stored in the dark at 4 degree °C and later transported on to the SEAES University of Manchester.

Human hair and nails samples were also collected from the volunteers along with their consent and stored properly in zip lock plastic bags to avoid any contamination.

5.4. Washing and cleaning procedure

Visible dirt was removed from the nail samples using a nylon wire brush and deionized water. Then 1% Triton-X100 solution was used and sonicated for 20 minutes. The wash solution was discarded and the nails were rinsed at least 3 times with 18.5 MΩ deionized water before being dried at 60 °C.

Hair samples were washed with 25 ml acetone (analytical grade from Fisher brand), sonicated for 10 minutes and 25 ml of 18.5MΩ deionized water and sonicated for 10 minutes . The wash solution was discarded and the process was repeated two more times with water and then finally with acetone. After the last wash step, the hair samples were allowed to dry overnight at room temperature.

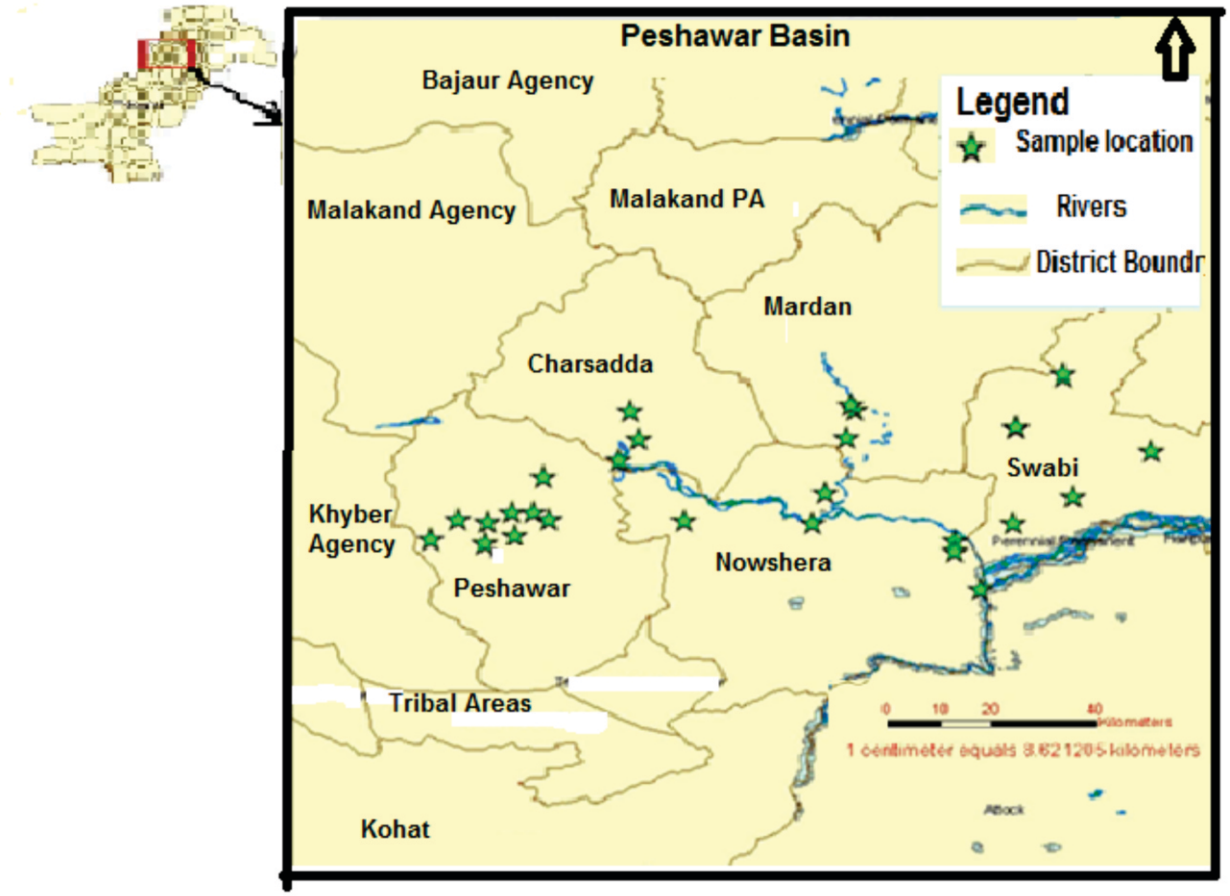

Fig. 2. Field areas and sample location map for Peshawar Basin KPK, Pakistan.

5.5. Field analysis

Calibrated portable probes (Hanna Water Test Meter, Whatman Conductivity m-Sensor) were used to measure the in situ pH, temperature and electrical conductivity of the drinking water samples in field.

5.6. Chemical analysis

Water samples were analyzed for total arsenic by ICP-MS (Plasma Quad II (Fissions). Operating conditions for the instrument were the same as described by Gault et al. (2005). Arsenic was detected at m/z = 75 with mass interference from $^{40}Ar^{35}Cl^{+}$ corrected through monitoring of m/z = 77 and 82 using TJA Solutions' Plasma Lab software. All the samples were run in duplicate and the standards were run after every set of 10 samples. Concentrations were determined using a 5 point calibration curve.

ICP-MS is useful for those samples having very low arsenic as its detection limit for most of the elements is typically below 0.01ng/ml. It is also preferred for its rapid analysis i.e., 60 seconds per samples and multi element analysis capability in a single run. In addition to its high sensitivity detection, it has the ability to measure a large range of concentration (Gill, 1997).

5.7. Quality control measures

Standards reference material (SRM), SRM NIST1640 for drinking and cooking water, and human hair CRM NCS DC 73347 was used during analysis. External standards and reagent blanks (acid blanks and Milli Q water blanks) were analyzed after every ten samples analyzed and duplicate samples were run in order to check the preparative steps applied during sample preparation.

An in house Turbo Pascal program, used for the drift correction of the raw instrumental data obtained from the ICP-MS, DBSCORR program was used for the correction of raw instrumental arsenic analysis

and were corrected for blanks, drift and analytical sensitivity using a least square fitting of a linear calibration of replicate analysis of five calibration standards (Polya, 2002a).

For IC- ICP-MS analysis, peak areas for individual arsenic species, were integrated by using TRPEAK software (Polya, 2002b).

5.8. Data analysis and data presentation

Different statistical techniques were applied for the data analysis and data presentation. SPSS, Microsoft Excel 2003, 2007 and Arc GIS9 were used for data presentation.

6. Results and discussions

All the physical parameters , such as, pH, temperature, conductivity etc. were analyzed on the spot at sources of drinking/cooking water (Table 1). The pH range is 7.6 to 9.1 with mean (7) and median (7) in the test samples suggest a slightly alkaline nature of water sources. There is a normal variation in the pH and EC. Previously (Shahida, 2007) also reported the alkaline nature of ground water.

The arsenic concentration ranged from 0.1-8 µg/L with a mean value of 0.9 µg/L and an average value 1.56 µg/L (SD=1.7) in this study (Table 2). This result for arsenic concentration in the drinking and cooking water of different parts of Peshawar basin i.e. Charsadda, Nowshera, Peshawar, Mardan and Swabi is in agreement with the already reported values of PCRWR, 2006-2008 for other KPK areas, viz. Peshawar, Mardan and Mingora and is also less than the WHO (10 µg/L) recommended guideline value for arsenic concentration for drinking water.

Possible reason for the low concentration of arsenic can be the depth and geology of water source (wells and bore holes). The majority of the samples are collected from Public Health and Engineering Department (PHED) tube wells which are very deep and the availability of favorable environment for the release of arsenic is comparatively less. The average depth of a bore hole in Pakistan is 115 ft according to the International Water Management Institute.

Table 1. Results for physical parameters for ground water used for drinking/cooking in KPK.

	Min	Max	mean	Median	SD
pH	6.94	7.20	7.01	7.00	0.05
Temp (C°)	25.90	27.4	26.9	27.0	0.30
Cond (µS/cm)	6.80	970	666	722	174
Eh (mV)	6.80	3.90	0.34	0.60	2.09

Table 2. Results of arsenic exposure for the volunteers of Peshawar basin, KPK.

	Minimum	Maximum	Mean	Std. Deviation
Age-Yrs	18.00	65.00	28.33	13.14
Weight-kg	46.00	85.00	60.52	9.21
BMI-Lbs/Inch^2	15.40	39.05	23.08	5.34
Water As (µg/L)	0.20	8.00	1.79	1.88
Hair As (mg/L)	0.02	0.37	0.12	0.09
Nails As (mg/L)	0.02	0.75	0.19	0.17
CDI water (µg/kg-BW)	0.01	0.29	0.06	0.07

The biomarkers of arsenic exposure like urine, hair and nail analysis for absorbed dose of arsenic is now considered as very important tool for identifying at risk groups. Biomarkers exposure data are more superior to the one collected by the use of questionnaire survey as it gives the exact picture of the absorbed dose in the biological system from all sources of exposure (Karagas et al., 2001a).

Arsenic in scalp hair, finger and toenails is being considered useful biomarkers for measurement of chronic arsenic exposure. Due to the binding of arsenic to keratin of hair and nails they give an idea about long term exposure to arsenic contamination (Slotnick and Nriagu, 2006; Slotnick et al., 2007).

The contents of arsenic in hair (mean value of (0.12 mg/Kg) and both hand and toe nails (mean value of (0.19 mg/Kg) are very much less than the values obtained for the exposed population in West Bengal India by Samantha et al. 2004 and by Gault et al 2006 in Combodia (Gault, 2008 ; Samanta, 2004; Anwar, 2005).

7. Risk assessment

During the field survey at least one principal user of each water source was interviewed in the national language, Urdu, and body mass index (BMI, kg/m2) was also calculated for him/her. Chronic daily intake (CDI µg/kg/body wt.) for each individual was calculated on the basis of this provided information. USEPA (1989) one hit model was used to estimate excess life time cancer risk due to arsenic intake from ground water and rice.

The calculated mean values for chronic daily intake from drinking water (0.06 µg/Kg-BW), is far less than the same values calculated for arsenic exposed area of West Bengal and Banglesh (Boyce, 2008; Polya, 2010; Rahman, 1996; Rahman, 2009).

The overall results were within the maximum contamination level values for arsenic contents of drinking water, which is actually beneficial for the residents of Peshawar, Mardan, Nowshera Charsadda and Swabi. This is the first study using human biomarkers of arsenic exposure in this area. Previously PCRWR (2003-2004) also reported no anomalous values for arsenic from Peshawar and Mardan which is in accordance with our results.

8. Conclusion

The results show that the ICP MS analysis for the drinking ground water collected from the major districts of Peshawar basin were within the permissible limits for arsenic below the WHO (10 µg/L) recommended guideline value for arsenic concentration in drinking water. In addition, the value of arsenic concentration in human hair and nail samples are also much lower than that of arsenic exposed populations in different parts of the world which further confirms our results.

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