ENVIRONMENTAL CONTAMINATION BY ARSENIC AND LEAD IN SOME RURAL VILLAGES IN INDIA

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ABSTRACT

This investigation focuses on the arsenic contamination problems in tube well groundwater systems and the different forms of arsenic and other toxic elements accumulated in human hair samples taken in a rural area of Allahabad, Utter Pradesh, India. The local residents at the study site depend on groundwater as their major source of household water. The oxidation reduction potential (ORP) and pH of groundwater samples were measured directly after the sampling of groundwater. Arsenic concentrations were measured directly in water samples by a colorimetric arsenic analysis kit after the water was pumped from a tube well and/or at a nearby laboratory. Human hair samples from the residents of the villages in the study site were analyzed by PIXE to measure a wide range of elements. An atomic absorption spectrometer was also used to measure arsenic concentrations. The results indicated that the concentrations of arsenic in groundwater and human hair were significantly higher in the village of Bada Kanjasa than in the villages of Kanua and Chota Kanjasa ($P<0.05$), clearly indicating that the higher arsenic concentration in groundwater reflected the accumulation of arsenic in human hair in the residents of Bada Kanjasa. The PIXE analysis also revealed an unusually high concentration of lead in human hair samples from Chota Kanjasa. Although the actual health effects and the detailed exposure mechanisms remain to be investigated, lead pollution is suspected to be the source of the exposure.

Keywords: PIXE, arsenic, lead, hair sample, ground water, environmental health

1. Introduction

Arsenic pollution causes health problems throughout the world through different exposure mechanisms. Citizens of the countries of India and Bangladesh, have shown chronic health problems due to their usage of arsenic-contaminated groundwater[1-2]. It is well known that arsenic-contaminated groundwater is a major source of chronic arsenic exposure, which causes the toxic effect known as arsenicosis, which involves skin abrasion, endocrine abnormalities, cancer and other health related problems. Since the arsenic compounds do not have strong taste or odor, people can be unaware of arsenic exposure; knowledge on the risks associated with arsenic exposure is important. The population groups most affected by arsenic exposure are those with low income and/or of lower education. A lack of knowledge about arsenic poisoning is considered to be a cause of the arsenic exposure in the abovementioned populations[3]. The installation of deep tube wells has a strong connection to arsenic contamination of groundwater due to the depth of the water catchment and geological materials. The installation of tube wells rapidly increased during 1980s with many international aid organizations, who aimed to decrease the mortality associated with waterborne diseases that are frequently encountered in open well water systems[1]. On one hand, the introduction of the tube wells, which acquired water from a more enclosed and deeper part of the ground, led to a decline in the incidence of waterborne disease-associated health problems. On the other hand, the water from acquired deeper groundwater reservoirs, which have lower oxygen levels, often contains a high level of dissolved forms of arsenic, including arsenite (III), which dissolve into the water more easily than other forms of arsenic. With an open well system, the most oxidized form of arsenic, arsenate (V), can become more dominant and it can bind with iron to form complex molecules of lower toxicity. Another fact is that many parts of India and Bangladesh are geologically rich in arsenic[2]. Our preliminary investigation in Allahabad, India indicated that level of arsenic exceeded the permissible levels set by the WHO and Indian government of 10 and 50 parts per billion (ppb), respectively[1]. The levels of arsenic concentration in groundwater were found to vary significantly, even in water drawn from wells that were located in close proximity to one another; this hypothesized to be due to a complex mechanism involving the geological materials[4, 5].

The purpose of the present study was to examine the arsenic concentrations in groundwater and human hair samples in three small rural villages near Allahabad, India and to investigate the correlations between the two parameters to safeguard human health among the people of rural India. Since tube wells are the primary source of daily water for most people in this area, it is important to determine the levels of arsenic in both the groundwater and human hair samples. In this study, we performed a multi-elemental analysis using a PIXE (Particle Induced X-ray Emission) to obtain information on a wide range of elemental contaminants from a limited number of hair samples. Furthermore, an atomic absorption spectrometer was used to measure the concentrations of certain elements using the pre-acid digestion process.

2. Materials and Methods

The sample sites were three small villages, Kanua, Chota Kanjasa, and Bada Kanjasa near Allahabad, Uttar Pradesh, India. These three villages are located near the Yamna River. Their relative positions (from upstream to downstream) are Kanua, Chota Kanjasa, and Bada Kanjasa, with approximately 1.5 km between each of the villages. The satellite photo shown in Figure 1 indicates the sites of the sampled tube wells with pin marks. The numbers of the sampled tube wells from each village were Kanua (n=13), Chota Kanjasa (n=11), and Bada Knajasa (n=15). A river water sample was taken near Kanua Village.

The arsenic concentrations, pH, and Oxidation Reduction Potential (ORP) of water samples were measured in India with a calorimetric arsenic test kit Merckoquant® (Merck, Germany) and portable pH, ORP meter (Horiba, Japan). All of the tube well water samples were brought back to a laboratory in the Sam Higginbottom Institute of Agriculture, Technology & Sciences (SHIATS), Allahabad and the arsenic concentrations were determined with a Merckoquant® arsenic test kit within six hours after the samplings. In some of the tube well water samples, the arsenic concentration was measured using the Merckoquant® kit in the field immediately after sample collection to confirm that the delayed measurement at the SHIATS laboratory was not affecting the results. The measurements of the pH and ORP were conducted directly after the sampling due to the rapid changes of oxidation reduction potentials. The pH and ORP values were applied to estimate the oxidation status of arsenic in the well water samples.

All human hair samples were obtained at three villages near the well water measurement sites in Kanua (n=9), Chota Kanjasa (n=12), and Bada Kanjasa (n=13). The human hair samples were obtained as a part of an interview survey of the villagers. In brief, the populations of Bada Kanjasa, Chota Kanjasa and Kanua were 97%, 83% and 46% female, respectively. The human hair samples were autoclaved at 120 °C for 15 minutes then washed in an ultrasonic bath with double-distilled water for ten minutes sonication. The sonication process was then repeated with acetone for ten minutes. Hair samples were then sequentially dried in an oven at 35°C for at least six hours before the analysis. Since the number of hair samples was limited, they were sent back to the Nishina Memorial Cyclotron Center, (NMCC) under the Japan Radioisotope Association according to the methods of Sera et al. (1992)[6] and further analysis was conducted using the Atomic Absorption Spectrometer (AAS), AAnalyst 800 (Perkin-Elmer, USA) at Rakuno Gakuen University.

The hair samples were analyzed using PIXE to measure the wide range of trace elements at NMCC according to the methods of Sera et al. (1999 and 2002)[7,8] and Habib et al. (2002)[9]. Since the mass of hair samples was limited to orders of milligrams, the multi-elemental analysis by PIXE measurement was both suitable and necessary to obtain an overview of the levels of trace elements in the hair samples.

Student’s *t*-test was used to determine statistically significant differences. A P value of <0.05 was considered to be statistically significant.

3. Results

The results of the arsenic measurements at the three villages are indicated in Figures 2-4 with concentrations and sample numbers in text, average values (in box plots), standard errors of the mean (in whisker plots), and levels of statistical significance (asterisks). The results of the arsenic measurements in Figure 2 indicated that the arsenic level was significantly higher in Bada Kanjas (71.1 ppb) than in the Kanua (5.0 ppb) and Chota Kanjasa (3.5 ppb). The measurement results from the AAS hair sample analysis are indicated in Figure 3 with concentrations and sample numbers in text, average values (in box plots), standard errors of the mean (in whisker plots), and levels of statistical significance (asterisks). The results indicated that the concentration of arsenic in the hair samples from Bada Kanjas (1687 ppb) was significantly higher than the concentration in hair samples from the Kanua (656 ppb) and Chota Kanjasa (555 ppb) villages. For the statistical analysis, we deployed data only by AAS and excluded PIXE results because the PIXE detected arsenic only for four specimens. This is to secure the precision of the statistical analysis. From these results, it can be seen that the high arsenic concentrations in tube well water affected the arsenic concentrations in villagers' hair. In this investigation, we did not survey individual water consumption practices in detail, thus the precise route of exposure is difficult to estimate. Further investigation, which provides more detail on the route of arsenic exposure, is necessary to perform a better health assessment.

Table 1. indicates the average values with standard deviation ($\pm 1\sigma$) of the ORP and pH levels from tube well water samples and one Yamuna river water sample. All of the groundwater samples showed average ORP values in the range of -106 to -80 mV in comparison to the river water sample, which showed +57 mV; all of the groundwater samples could therefore said to contain reduced ORP. The average pH values for the groundwater samples were between 7.0 and 7.3, while the pH of the river water was 8.1. Figure 5. indicates a plot of the expected oxidation status for arsenic derived from Nernst equation using the ORP and pH values. The measured ORP and pH values of the groundwater samples are illustrated with dots on this plot. From these measurements, all of the tube well water samples were considered to be under oxygen reduced conditions with arsenic existing in the form of arsenite (III). In contrast, arsenic in the river water was present as arsenate (V).

The interviews with the local villagers revealed no serious health problems; however, given that only approximately 30-40% of the villagers visit a local health clinic, there might be some underlying problems of unknown cause. While acute arsenic poisoning is a well-established toxicological phenomenon, chronic arsenic poisoning may have various symptoms, which makes its differential diagnosis difficult[10]. Furthermore, the people who participated on this survey were only there on a volunteer basis and the participants might not have accurately represented the health conditions of the whole populations. For future investigations, it might be necessary to include the population of an entire village population and/or apply random selection to the interviewees through such methods as door to door visits to conduct the survey.

The purpose of using PIXE measurement was to determine multi-elemental concentrations with a small number of hair samples. This investigation was initiated to determine the arsenic concentrations; however, the PIXE analysis also revealed a noticeably high concentration of lead in the hair samples from Chota Kanjasa. Figure 5 indicates the average concentrations of lead with concentrations and sample numbers in text, average values (in box plots), standard errors of the mean (in whisker plots), and levels of statistical significance (asterisks).

4. Discussion

The significant finding is that the concentrations of lead in the hair samples from Chota Kanjasa (822 ppm) were much higher than the highest levels of lead sampled in Japan (1.1-22.9 ppm), which were obtained in the Tokyo metropolitan area in 1976 to 1985, and which were attributed to the widespread use of leaded gasoline as fuel for automobiles[11]. A simple comparison with the highest lead concentration value from metropolitan Tokyo (22.9 ppm), shows that the values from Chota Kanjasa and Bada Kanjasa are about 36 times and 4 times higher, respectively, which are rather alarming levels. A statistical analysis indicated that the concentration of lead in Chota Kanjasa was significantly higher than that in Bada Kanjasa. This must be due to a regional difference. Common sources of lead contamination include the use of lead drinking water pipes, leaded paint, and leaded gasoline. Exposures can occur via the direct intake of water, air, and dust, or indirect intake from food such as vegetables, meat and dairy products. A possible source of the lead pollution may be a nearby power plant. Although there were no air-quality measurements at the villages in the study site, coal can contain lead and without good after treatment of exhaust, the combustion process can release particles with high concentrations of lead into the atmosphere. The significantly lower value of lead at Bada Kanjasa, may be explained by wind patterns and the local topography. It is necessary to monitor the air quality of the three villages and to perform meteorological measurements at a local scale to understand the movement of the air pollution. In the case of Kanua village, the concentrations of lead varied to a greater extent. This can be explained by the differences in the exposure patterns of individuals. Since there were more male residents who participated in this survey, lifestyle factors such as working outside of the village might have been an important factor. Furthermore, the combined health effects of arsenic and lead may be a possible health risk among the local people; although a full health assessment was beyond the scope of this study.

PIXE measurement allowed us to reveal a possible lead poisoning problem in three rural villages of India. Since the lead poisoning may affect the children to a greater extent than adults, it is necessary to further investigate lead exposure of children in the villages and to determine the source or sources of lead emission. The possible existence of multiple exposure pathways should be carefully investigated to protect the villagers from arsenic and lead-related health problems. A further survey with clinical investigation with the involvement of physicians might provide a more effective method for elucidating the current levels of pollution and the state of health in the study area.

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References:

1. Arsenic, Fact sheet No. 372, World Health Organization, www.who.int/mediacentre/factsheets/fs372/en/, accessed 2015. 02. 08.

2. Mukherjee, A., Sengupta, M.K., Hossain, M.A., Ahamed, S., Das, B., Nayak, B., Lodh, D., Rahman, M.M., Chakraborti, D., Arsenic contamination in groundwater: a global perspective with emphasis on the Asian scenario, *J Health Popul Nutr.*, 24(2), (2006) 142-63.

3. A. Sarkar, Ecosystem perspective of groundwater arsenic contamination in India and relevance in policy, *EcoHealth*, 7(1), (2010) 114-26.

4. Ferguson, J.F. & Gavis, J., A review of the arsenic cycle in natural waters, *Water Res*, **6**: (1972) 1259–1274.

5. Winkel, L. H. E., Trang, P. T. K., Lan, V. M., Stengel, C., Amini, M., Ha, N. T., Viet, P. H., and Berg, B., Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century, *Proc. Natl. Acad. Sci.,* 108(4), (2011) 1246–1251.

6. Sera, K., Yanagisawa, T., Tsunoda, H., Futatsugawa, S. Hatakeyama, S. Suzuki, S. and Orihara,H., The Takizawa PIXE Facility Combined with a Baby Cyclotron for Positron Nuclear Medicine, *Int'l Journal of PIXE* Vol. 2(1), (1992) 47-55.

7. Sera, K., Futatsugawa, S. and Matsuda, K., Quantitative Analysis of Untreated Bio-samples, Nuclear Instruments and Methods in Physics Research B 150, (1999) 226-233.

8. Sera, K., Futatsugawa, S. and Murao S., Quantitative Analysis of Untreated Hair Samples for Monitoring Human Exposure to Heavy Metals, *Nuclear Instruments and Methods in Physics Research* B189, (2002)174-179.

9. Habib, M.A., Miono, S., Sera, K., and Futatsugawa, S., PIXE Analysis of Hair in Arsenic Pollution, Bangladesh., *Int'l Journal of PIXE*, Vol.12 (19), (2002) 19-34.

10. Casarett and Doull's Toxicology the basic science of poisoning 7th ed.; Klaassen, C.D., Ed.; Mc Graw Hill, 2008.

11. Matsuda, K., Tamura, M., Trace elements found in human hair (in Japanese without abstract), Japan Environmental Science center annual report 12, 13, (1986) 101-110.

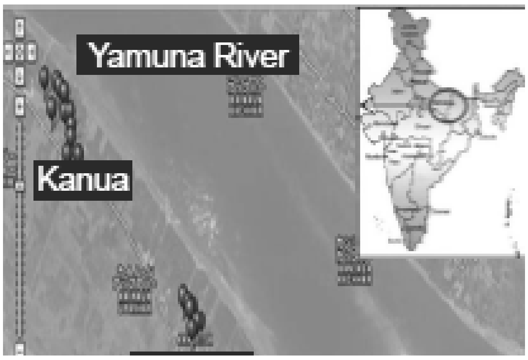

Figure 1: a) Map of India with circle for the city of Allahabad and more enhanced satellite image for investigated sites. The pins indicate the sampled tube wells.

Table 1. The average (±1 σ) of ORP and pH values for investigated well waters and a Yamuna River water sample.

	Location			
	Kanua	Chota Kanjasa	Bada Kanjasa	Yamuna River
ORP (mV)	- 105 (± 11)	- 80 (± 46)	- 106 (± 36)	57
pH	7.2 (± 0.1)	7.0 (± 0.2)	7.3 (± 0.1)	8.1

ORP: Oxidation Reduction Potential

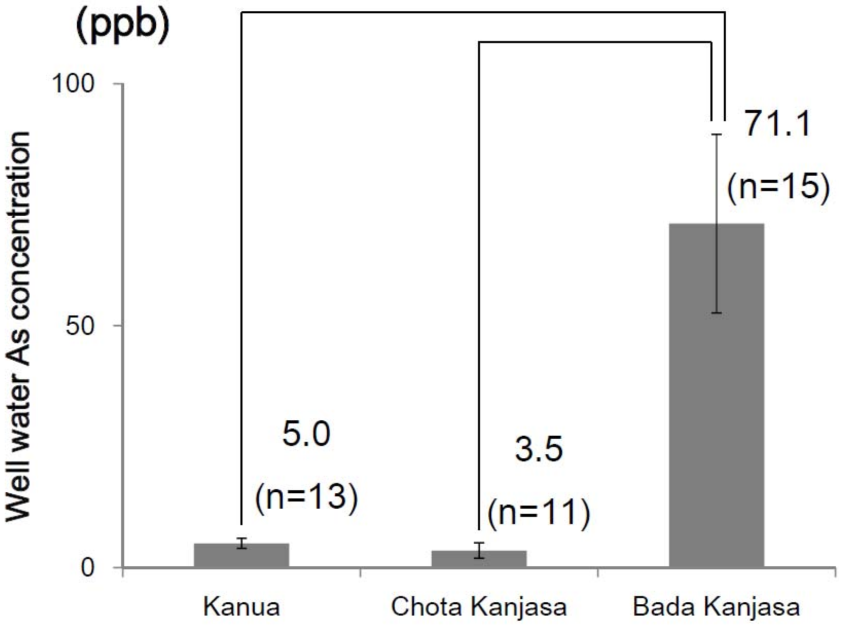

Figure 2. The arsenic concentrations in the groundwater samples from the villages in Allahabad. The box plots indicate the average arsenic concentrations and the whisker plots indicate the standard error of the means. The average concentrations and sample numbers (n) are indicated on top of the box plots of the standard error of the means. *: $P<0.05$

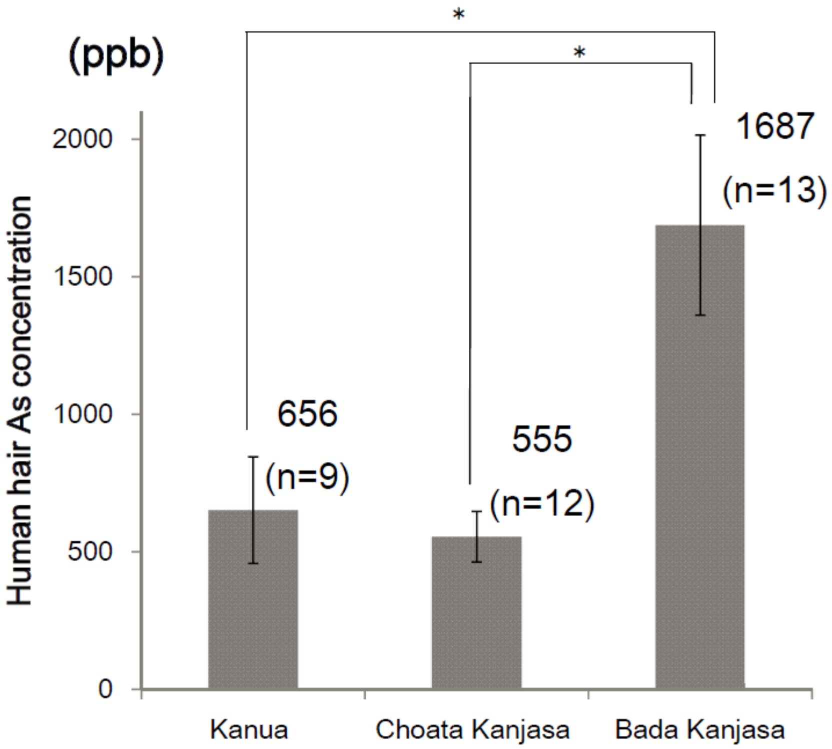

Figure 3. The arsenic measurement results from human hair samples from the villages in Allahabad. The average concentrations are indicated in boxes and numbers, the sample numbers (n), and Standard error of the means are plotted on whisker plots. *: *P*<0.05

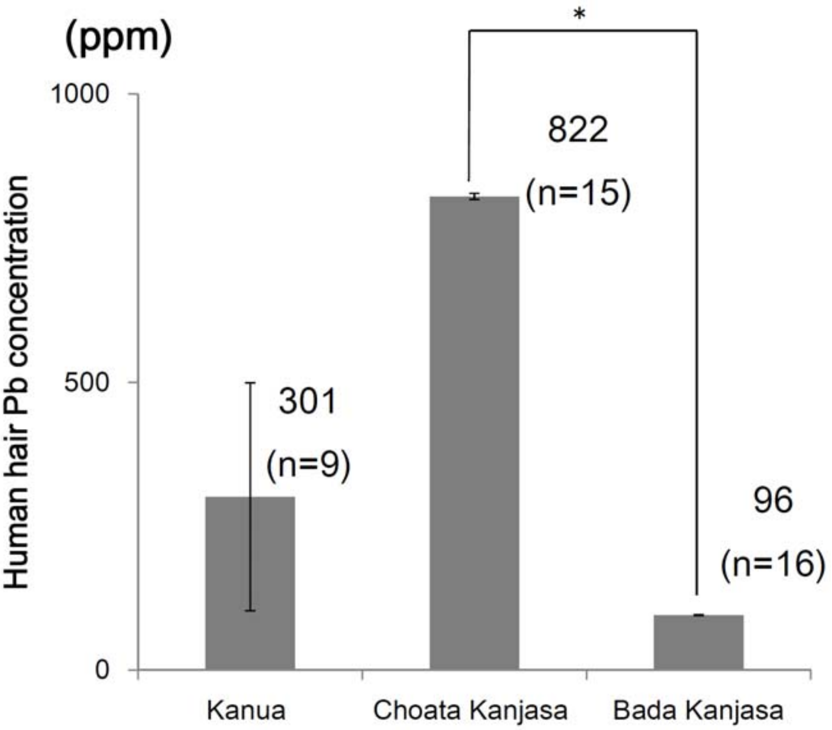

Figure 4. Lead measurement for human hair samples results from the villages in Allahabad. The average concentrations are indicated in boxes and numbers, sample numbers (n), and the Standard error of the means are plotted on whisker plots. *: $P<0.05$

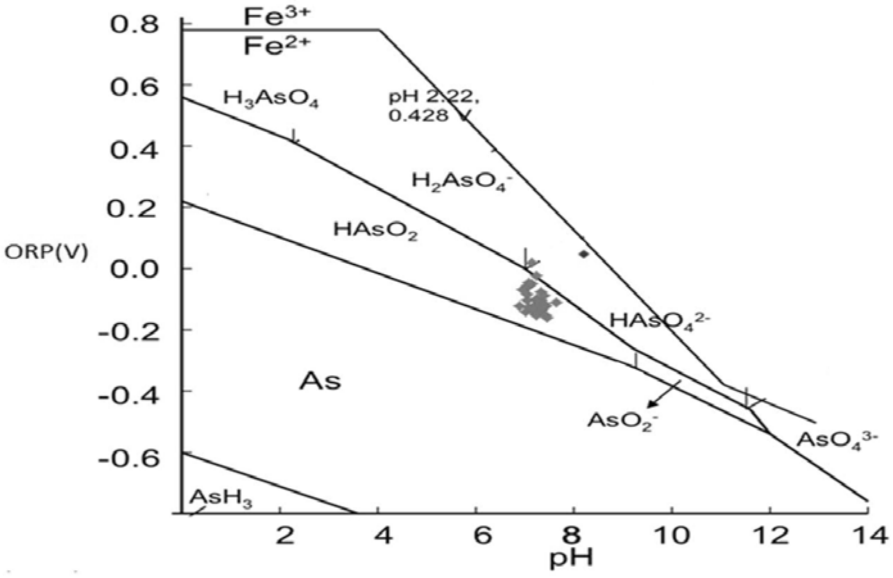

Figure 5. The plot derived from the Nernst equation at given range of ORP and pH values for arsenic. A cluster of dots in the middle indicates the tube well water samples and single dot indicates the river water sample. From the plot, arsenite (III) is expected form the arsenic found in tube well waters and arsenate (V) is expected from the river water sample.