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Occurrence and Severity of Arsenic in Urine, Hair and Nails Through Contaminated Drinking Water in Pakistan

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Abstract. The study on contamination of well waters of Hyderabad city with arsenic and its effect on urine, hair and nails of people consuming this water revealed the concentration of arsenic in well waters to be 25.413 to 1286.47 ppb and that in urine of the people to be 2.032-33.906 ppb, in hair 105.7-427.96 ppb and in nails 8.579-71.033 ppb.

Keywords: Pakistan, groundwater, arsenic contamination, Hyderabad city

Introduction

Arsenic has long been classified as a poison. This odourless and tasteless substance, when ingested at high concentrations, may cause death, whereas lower levels of exposure to arsenic can yield detrimental results such as cancer and a number of other diseases. The most common route of arsenic into human body is through ingestion of contaminated drinking water (NRC, 1999).

Arsenic in groundwater results from water-rock interaction, leaching of mine tailings and from arsenic rich fumes infiltrating through the soil (Armienta *et al*., 1997). Arsenic is typically released to the environment in an inorganic form, and it tends to adsorb strongly to soil which may either run off into surface water bodies or leach into shallow groundwater.

If exposure of an individual to arsenic is suspected, examination of biomarkers can provide useful information The most commonly used biomarkers are hair, nails, blood and urine. The use of these indicators, however, is not without problems, with hair and nails being particularly prone to external contamination. In humans, the gastrointestinal tract absorbs 60-90% of ingested soluble arsenic. Acute arsenic poisoning results in vomiting, oesophageal and abdominal pain, bloody urine, diarrhoea, anuria, shock, convulsions, coma and death (Hughes, 2002). Chronic exposure to arsenic can lead to detrimental effects involving skin, lung, liver and bladder cancer, diabetes and vascular diseases, as well as pregnancy irregularities including stillborns and spontaneous abortions (Armienta *et al.*, 1997; Gorby, 1994).

Humans eliminate most of the ingested arsenic (e.g., 40-80% of ingested arsenite or arsenate) through urine. Generally, 40-60% of the daily intake of inorganic arsenic is excreted each day in urine (Farmer and Johnson, 1990; Buchet *et al*., 1981). Normal arsenic values in urine range from 0.005 to 0.04 ppm (Takagi *et al*., 1988; Narang *et al*., 1987). The concentration of total arsenic in urine is generally used and accepted as a good and recent indicator of the absorbed amount of arsenicals (Vahter and Lind, 1986). However, contradictory findings have been recorded regarding the correlation of arsenic intake and its concentration in human urine.

Arsenic concentrations are normally higher in hair and nails than in other parts of the body because of the high content of keratin, which might bind trivalent inorganic arsenic (Hostýnek *et al*., 1993; Curry and Pounds, 1977; Hopps, 1977). The concentration of arsenic in the root of the hair is in equilibrium with the concentration in the blood. Hair might be considered an excretory pathway; once incorporated in the hair, arsenic is not biologically available. Arsenic poisoning may have hair concentrations varying, from 10 ppm to 100 ppm. In people with no known exposure to arsenic, the concentration of arsenic in hair is generally 0.02-0.2 mg/kg (Kurttio *et al*., 1998; Rogers *et al*., 1997; Paulsen *et al*., 1996; Vienna *et al*., 1995; Wolfsperger *et al*., 1994). Hair arsenic levels can provide useful information in chronic arsenic poisoning. However, the ingested arsenic and that derived from external contamination are both bound to the outer surface of the hair and these two sources cannot be differentiated by any known technique.

Normal arsenic values in nails appear to range from 0.02 to 0.5 ppm (Takagi *et al*., 1988; Narang *et al*., 1987). A single dose of arsenic can be detected at the distal tip of the nails about 100 days after exposure (Pirl *et al*., 1983). Presumably, arsenic is deposited in the nail roots from the blood and then migrates distally as the nails grow (at about 0.12 mm a day).

Arsenic concentration in hair and nails might increase as a result of surface contamination. The source of arsenic on the outer surface of hair is claimed to be both ingestion and

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*Author for correspondence; E-mail: ameerakhan07@yahoo.com external contamination, such as via air, water, soaps/shampoos etc. which may produce arsenic concentrations of several thousand ppm and therefore can mislead investigators attempting to diagnose chronic arsenic poisoning (Hindmarsh and McCurdy, 1986).

The present study is a cross sectional research on the suspected contamination of the ground water (well water) of Hyderabad city of Pakistan with arsenic and arsenic concentration in hair, nails and urine of the residents of the city who had been consuming such water from wells since decades; these people had manifested typical symptoms of acute arsenic poisoning.

Materials and Methods

Samples of nails, hair and urine of the people suffering from the typical symptoms of arsenic poisoning as well as the well water used by them for drinking purpose were tested in triplicate for arsenic concentration. Samples of water were analyzed with standard reference material. Recovery test for arsenic in 3 samples of drinking water and 2 samples of urine, hair and nails was also performed.

Hair and nail samples were washed twice with deionized water (5 ml) and then methanol (5 ml) to reduce any external material without leaching arsenic out of the hair and nails. Samples were dried and digested by boiling in a mixture of nitric/perchloric/sulphuric acids for 3 h until the acid evaporated. The remaining volume was reconstituted to 25 ml with deionized water and an aliquot was analyzed. Samples of urine and water were analyzed by wet digestion method with concentrated nitric acid. Total arsenic was detected by continuous-flow hydride generation atomic absorption spectrometry (AAS) using Atomic Absorption Spectrophotometer (Hitachi Model Z-5000), equipped with Zeeman background corrector and data processor, ZAA and Hydride Formation Unit (AOAC, 1990). Working conditions adopted during analysis of arsenic are given in Table 2.

Results and Discussion

Arsenic has long been known to be toxic to humans and has been classified as a human carcinogen (IARC, 1987). The greatest health concern with regard to regular exposure to arsenic derives from consumption of drinking water containing elevated concentrations of arsenic which is a major pathway into the human body. The WHO guideline for arsenic in drinking water is 10 ppb (WHO, 1999) which is exceeded in many areas of the world. However, the US Environmental Protection Agency (2000) has suggested that the concentration of arsenic in drinking water should be no more than 5 or even 2 ppb. Other existing standards for arsenic in drinking water are given in Table 1.

Working conditions of the procedure used in the study are described in Table 2, whereas accuracy of the procedure was determined through comparison with standard reference material (Table 3). For further rectification of any discrepancy, arsenic was added to the samples and percentage recovery was determined (Table 4 and 5).

Concentration of arsenic in ten samples of well water used as drinking water in Hyderabad city revealed that arsenic concentration in all the samples were above the permissible standard (Fig. 1); statistics are given in Table 6. Concentration of arsenic was low in some samples of well water and too high in others. This might be due to solubility of arsenic in water, time of digging of well or geology of underground water of wells. Such high values are dangerous for the health of the people consuming such water as well as occupational risk related to their use in agriculture (Hinwood *et al*., 2003).

Table 1. Existing standards of arsenic in drinking water

International Standards	Maximum permissible limit
World Health Organization (WHO)	10 ppb
US Environmental Protection Agency (US EPA)	10 ppb
Bangladesh Standards (BSTI)	50 ppb
Pakistan Standard Quality Control Authority (PSQCA)	10 ppb
Indian Standards (IS)	50 ppb

Table 2. Working conditions adopted for determination of arsenic

Element	Wavelength (nm)	Slit (nm)	Flame composition	Reductant channel	Acid channel
Arsenic	193.7	0.5	Air-acetylene	1% $NaBH_4$, 20% KI	1.2N HCl

Table 3. Accuracy and precision of analytical procedure (standard reference material: trace elements in natural water SRM-1640)

Element	Certified conc. (ppb) (Mean value ± SD)	Observed conc. (ppb) (Mean value ± SD)	Number of determinations	RSD (%)
Arsenic	26.67 ± 0.41	26.384 ± 0.205012	5	0.77

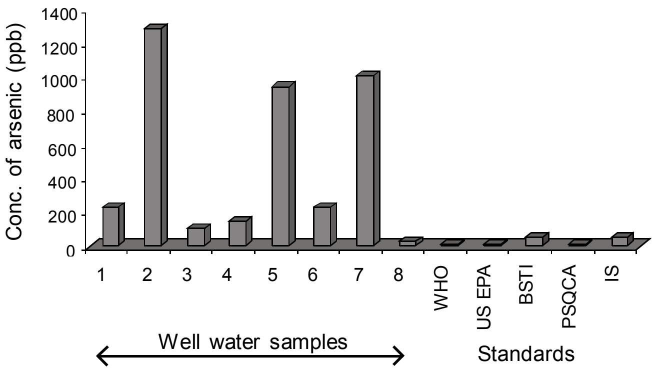

Fig. 1. Comparative overview of arsenic in well water with existing standards.

Table 4. Recovery of arsenic added in 2 samples of urine, hair and nails each

Matrix	Spiking level (ppb)	Mean detected conc. (ppb)	Recovery (%)	± SD
Urine	5.0	4.895	97.90	0.014849
	5.0	4.916	98.32	
Hair	2.0	1.945	97.25	0.031113
	2.0	1.989	99.45	
Nail	0.5	0.487	97.4	0.002828
	0.5	0.491	98.2	

Table 5. Recovery of arsenic added in 3 samples of well water

Actual conc. (ppb)	Detected conc. (ppb)	Recovery (%)	± SD
0.5	0.474	94.8	0.008
0.5	0.482	96.4	
0.5	0.490	98.0	

Different biomarkers reflect different timescales of exposure to arsenic; hair and nails reflect past or long-term exposure, while blood and urine levels reflect recent exposure. Concentration of arsenic in 10 samples of urine, hair and nails are shown in Fig. 2 and statistics is given in Table 6. Measurement of total arsenic in urine needs to be treated with caution as a large proportion of this could be relatively non-toxic organic forms. Though high arsenic concentration in the urine is indicative of continued exposure to arsenic, it is not always diagnostic of chronic arsenic toxicity. (Chowdhury *et al.* 1997). There have been contradictory findings in respect of the correlation of the intake of arsenic-contaminated water and corresponding concentration of arsenic in urine. Our findings also do not show a good correlation between arsenic in water to that in urine (Fig. 3).

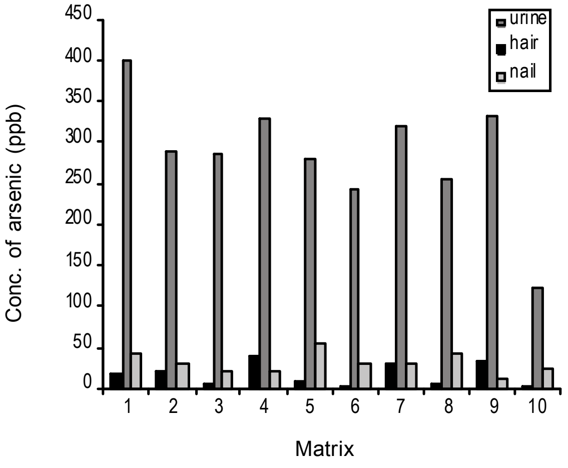

Fig. 2. Arsenic found in patients.

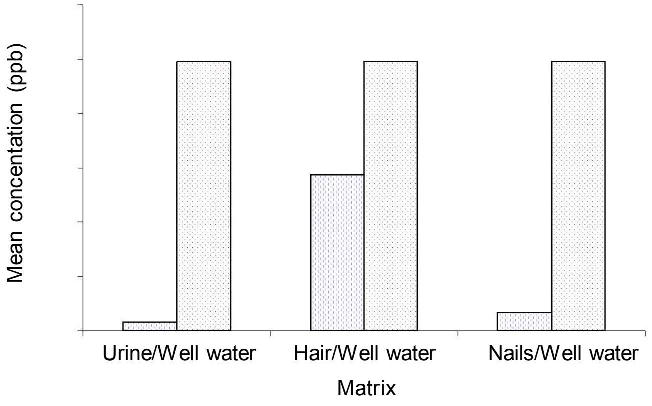

Fig. 3. Comparision of arsenic in urine, hair and nails with that in well water.

Table 6. Statistical analysis of arsenic in urine, hair, nails and well water

Matrix (ppb)	No. of samples	Range	Mean	Median	±SD	RSD%
Urine	10	2.032-33.906	16.606	18.0505	0.008	0.061
Hair	10	105.7-427.96	286.52	329.395	0.003	0.033
Nails	10	8.579-71.033	32.605	30.570	0.003	0.010
Water	08	25.42-1286.68	496.683	232.215	0.050	0.014

Hair and nails suffer from contamination problems and it is difficult to ascribe what is likely to be due to external exposure. Some workers have suggested that human hair and nails can give estimates of arsenic body load (Chowdhury *et al*., 1997). In some other cases, there was no accordance between hair arsenic content and total life intake. The most probable explanation of this finding is that of external contamination due to the use of contaminated water for washing purposes. However, most of the studies favour a correspondence between the amount of arsenic in drinking water and that in hair. (Das *et al*., 1995; Borzsonyi *et al*., 1992; Hindmarsh and McCurdy, 1986; Valentine *et al*., 1979; Harrington *et al*., 1978; Grantham and Jones, 1977). According to the results of above studies, arsenic concentration of hair can be used as a good measure of past exposure to arsenic via drinking water. In our study, most of the patients had arsenic concentrations in hair from 50 to 100 ppb, a few persons showed concentrations over 150 ppb and some had near 500 ppb.Thus a good relationship between arsenic concentrations in drinking water and in hair of patients was observed (Fig. 3). Patients who take drinking water with average arsenic concentration of 496.683 ppb had average arsenic concentration of 286.52 ppb in hair. Our findings showed that hair arsenic concentration can be used as a good proxy for chronic arsenic ingestion via drinking water.

Data on arsenic in nails are sparse. There appears to be no fixed maximum limit for the amount of arsenic that can be absorbed in body organs so it is not necessary that arsenic accumulates equally in hair and nails. (Agahain *et al*., 1990; Gonzales *et al*., 1954). Large amounts of arsenic have been reported in cases of chronic arsenic poisoning (Das *et al*., 1995). The average concentration of arsenic for our reference group was 8.579-71.033 ppb (Table 4); in our findings, no significant correlation between arsenic in nails and water was seen.

References

Agahain, B., Lee, J.S., Nelson, J.H., Johns, R.E. 1990. Arsenic levels in fingernails as a biological indicator of exposure to arsenic. *Am. Ind. Hyg. Assoc.* **51:** 646-651.

AOAC. 1990. *Official Method of Analysis*, 15th edition, Association of Official Analytical Chemists, Washington DC., USA.

Armienta, M.A., Rodriguez, R., Cruz, O. 1997. Arsenic content in hair of people exposed to natural arsenic polluted ground-water at Zimapan, Mexico. *Bull. Environ. Contam. Toxicol.* **59:** 583-589.

Borzsonyi, M., Berecsky, A., Rudnai, P., Csanady, M., Horvath, A. 1992. Epidemiological studies on human subjects exposed to arsenic in drinking water in southest Hungary. *Arch. Toxicol*. **66:** 77-78.

Buchet, J.P., Lauwerys, R., Roels, H. 1981. Comparison of the urinary excretion of arsenic metabolites after a single dose of sodium arsenite, monomethylarsonate of dimethylarsinate in man. *Int. Arch. Occup. Environ. Health* **48:** 71-79.

Chowdhury, T.R., Mandal, B.K., Samanta, G.K., Basu, G.K., Chowdhury, P.P., Chanda, C.R., Karan, N.K., Lodh, D., Dhar, R.K., Das, D., Saha, K.C., Chakraborti, D. 1997. Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world: the status report up to August 1995. In: *Arsenic Exposure and Health Effects*, C. O. Abernathy, R. L. Calderon and W. R. Chappell (eds.), pp. 93-111, Chapman and Hall, London, UK.

Curry, A.S., Pounds, C.A. 1977. Arsenic in hair. *J. For. Sci. Soc*. **17:** 37-44.

Das, D., Chatterjee, A., Mandal, B.K., Samanta, G., Chakraborti, D., Chanda, B. 1995. Arsenic in groundwater in six districts of West Bengal, India: The biggest arsenic calamity in the world. Part 2. Arsenic concentration in drinking water, hair, nails, urine, skin-scale and liver tissue (biopsy) of the affected people. *Analyst* **120:** 917-924.

Farmer, J.G. , Johnson, L.R. 1990. Assessment of occupational exposure to inorganic arsenic based on urinary concentrations and speciation of arsenic. *Br. J. Ind. Med*. **47:** 342-348.

Gonzales, T.A., Vance, M., Helpern, J., Umberger, C. 1954. *Legal Medicine Pathology and Toxicology*, 2nd edition, Appleton-Century-Crafts, New York, USA.

Gorby, M.S. 1994. Arsenic in human medicine. In: *Arsenic in the Environment, Part-II: Human Health and Ecosystem Effects*, J. O. Nriagu (ed.), pp. 1-16, John Wiley & Sons Inc., New York, USA.

Grantham, D.A., Jones, J.F. 1977. Arsenic contamination of water wells in Nova Scotia. *J. Am. Water Works Assoc*. **69:** 653-657.

Harrington, J.M., Middaugh, J.P., Morse, D.L., Housworth, J. 1978. A survey of a population exposed to high concentrations of arsenic in well water in Fairbanks, Alaska. *Am. J. Epidemiol*. **108:** 377-385.

Hindmarsh, J.T., McCurdy, R.F. 1986. Clinical and environmental aspects of arsenic toxicity. *Crit. Rev. Clin. Lab. Sci.* **23:** 315-347.

Hinwood, A.L., Sim, M.R., Jolley, D., deKlerk, N., Bastone, E.B., Gerostamoulos, J., Drummer,O.H. 2003. Hair and toenail arsenic concentrations of residents living in areas with high environmental arsenic concentrations-Environmental Medicine. *Environ. Health Perspect.* **111:** 187-194.

Hopps, H.C. 1977. The biological bases for using hair and nail for analyses of trace elements. *Sci. Total Environ.* **7:** 71-89.

Hostynek, J.J., Hinz, R.S., Lorence, C.R., Price, M., Guy, R.H. 1993. Metals and the skin. *Crit. Rev. Toxicol.* **23:** 171-235.

Hughes, M.F. 2002. Arsenic toxicity and potential mechanisms of action. *Toxicol. Lett*. **331:** 1-16.

IARC 1987. Overall evaluations of carcinogenicity. An updating of IARC monographs 1-42. In: *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, Suppl. 7, International Agency for Research on Cancer, Lyon, France.

Kurttio, P., Komulainen, H., Hakala, E., Kahelin, H., Pekkanen, J. 1998. Urinary excretion of arsenic species after exposure to arsenic present in drinking water. *Arch. Environ. Contam. Toxicol*. **34:** 297-305.

Narang, A.P.S., Chawla, L.S., Khurana, S.B. 1987. Levels of arsenic in Indian opium eaters. *Drug Alcohol Depend*. **20:** 149-153.

National Research Council (NRC) 1999. *Arsenic in Drinking Water*, Sub-committee on Arsenic in Drinking Water, Committee on Toxicology Board on Environmental Studies and Toxicology Commission on Life Sciences, National Academy Press, Washington DC., USA.

Paulsen, F., Mai, S., Zellmer, U., Alsen-Hinrichs, C. 1996. Blood and hair arsenic, lead and cadmium analysis of adults and correlation analysis with special referene to eating habits and other behavioral influences. *Gesundheitswesen* **58:** 459-464.

Pirl, J.N., Townsend, G.F., Valaitis, A.K., Grohlich, D., Spikes, J.J. 1983. Death by arsenic: A comparative evaluation of exhumed body tissues in the presence of external contamination. *J. Anal. Toxicol*. **7:** 216-219.

Rogers, C.E., Tomita, A.V., Trowbridge, P.R., Gone, J.K., Chen, J., Zeeb, P., Hemond, H.F., Thilly, W.G., Olmez, I., Durant, J.L. 1997. Hair analysis does not support hypothesized arsenic and chromium exposure from drinking water in Woburn, Massachusetts. *Environ. Health Perspect*. **105:** 1090-1097.

Takagi, Y., Matsuda, S., Imai, S., Ohmori, Y., Masuda, T., Vinson, J.A., Mehra, M.C., Puri, B.K., Kaniewski, A. 1988. Survey of trace elements in human nails: An international comparison. *Bull. Environ. Contam. Toxicol*. **41:** 690-695.

US Environmental Protection Agency (2000). Drinking water priority rulemaking - Arsenic; accessed on 4/5/00 at URL http://www.epa.gov/OGWDW/ars/arsenic.html

Vahter, M., Lind, B. 1986. Concentrations of arsenic in urine of the general population in Sweden. *Sci. Total Environ*. **54:** 1-12.

Valentine, J.L., Kang, H.K., Spivey, G. 1979. Arsenic levels in human blood, urine and hair in response to exposure via drinking water. *Environ. Res.* **20:** 24-32.

Vienna, A., Capucci, E., Wolfsperger, M., Hauser, G. 1995. Heavy metals in hair of students in Rome. *Anthrop. Anz.* **53:** 27-32.

Wolfsperger, M., Hauser, G., Gossler, W., Schlagenhaufen, C. 1994. Heavy metals in human hair samples from Austria and Italy: Influence of sex and smoking habits. *Sci. Total Environ.* **156:** 235-242.

World Health Organization. 1999. Arsenic in drinking water: Fact Sheet 210, accessed on 4/5/00 at URL http://www.who.int/inf-fs/en/fact210.ht