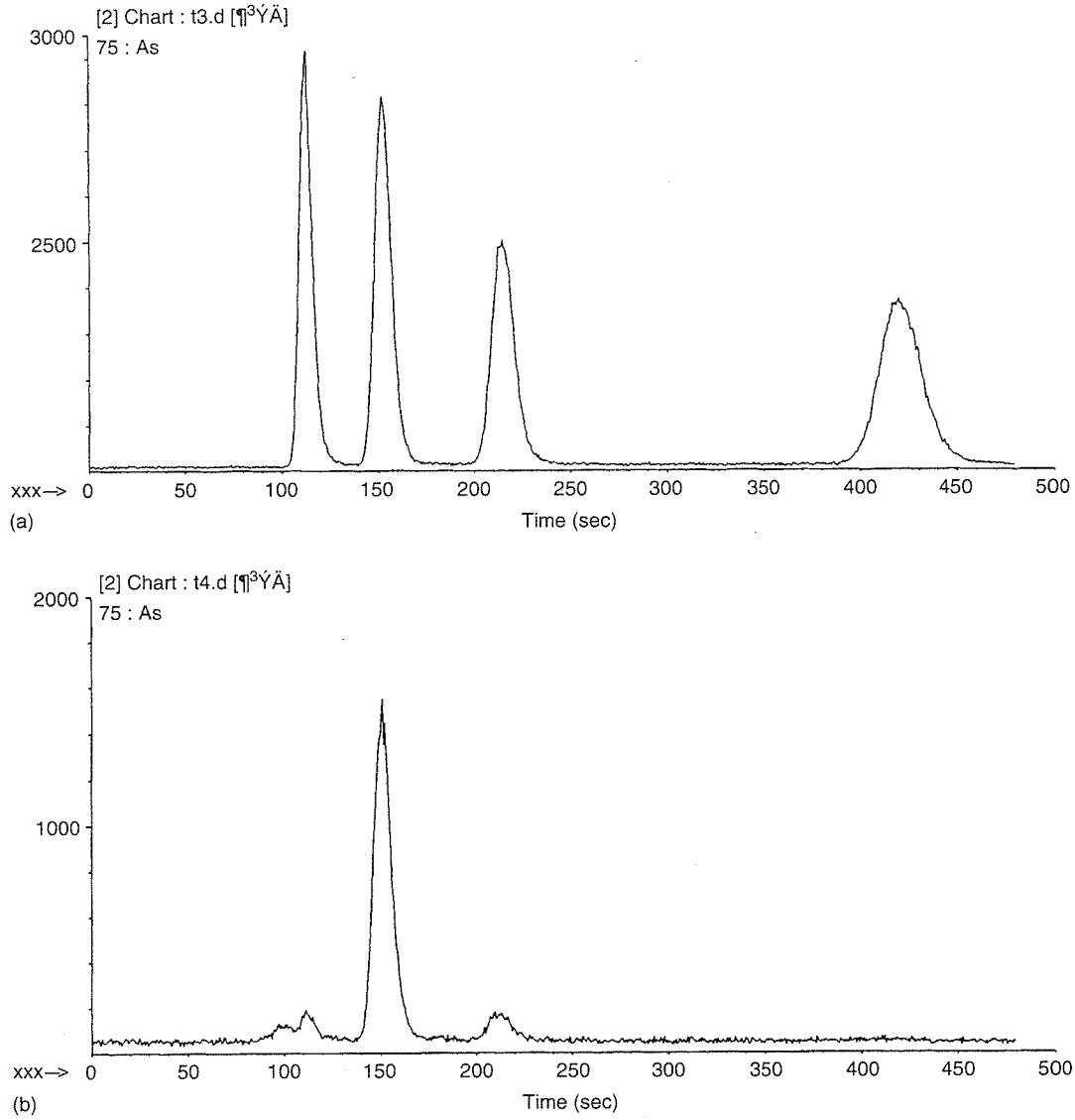


Figure 1. (a) HPLC chromatogram of arsenic(III), DMA, MMA and arsenic(V) at 150 ppb. arsenic(III): 113 s; DMA: 153 s; MMA: 215 s; arsenic(V): 421 s. (b) HPLC chromatogram of arsenic species in urine. HPLC conditions: detection, Agilent 7500 model ICP-MS (*m/z*: 75); column, Gel PAK-GL-IC-A15 (4.6 mm i.d. × 150 mm); mobile phase, 10 mM phosphate buffer (pH 6.0); column temperature, 35 °C; flow rate, 1 ml min^{-1}.

Table 3. Concentration of inorganic arsenic in tubewell water

	Tubewell	As(III) (ppb)	As(V) (ppb)	Total As (ppb)	As(III)/total As (%)
1	A (TW)	577.9	13.0	590.9	97.8
2	A (115 ft)	57.5	3.5	61.0	94.3
3	A (deep)	7.8	1.8	9.6	81.3
4	G (72 ft)	110.2	10.7	120.9	91.1
5	G (deep)	1.7	3.5	5.2	32.7
6	I (152 ft)	13.6	4.4	18.0	75.6
7	I (deep)	1.1	5.5	6.6	16.7
8	K (45 ft)	402.8	5.6	408.4	98.6
9	K (deep)	2.0	4.2	6.2	32.3

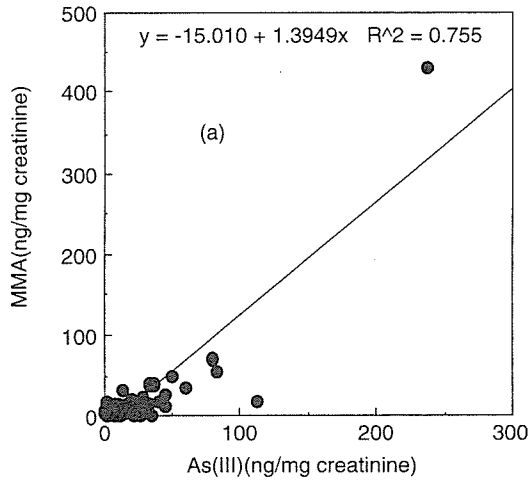
area consume freshwater shrimps. In our study we considered the total arsenic concentration in urine as the sum of arsenic(III), DMA, MMA and arsenic(V) concentrations, neglecting the presence of the small amount of arsenobetaine which clearly did not come from the arsenic-contaminated water. The concentrations of arsenic(III), DMA, MMA and arsenic(V) in the 44 urine samples ranged from <0.2 to 237.4 ng mg^{-1}, <0.2 to 2166.4 ng mg^{-1}, <0.2 to 430.6 ng mg^{-1} and <0.2 to 89.7 ng mg^{-1} creatinine respectively. The respective averages are 28.7 ng mg^{-1}, 168.6 ng mg^{-1}, 25.0 ng mg^{-1} and 4.6 ng mg^{-1} creatinine. The woman identified as K-1, who is 40 years old, excreted the highest amount of total arsenic, at 2890.0 ng mg^{-1} creatinine, in her urine. The arsenic concentration in the shallow tubewell water used by the K family

Table 4. Urinary creatinine and arsenic species obtained from families A to M

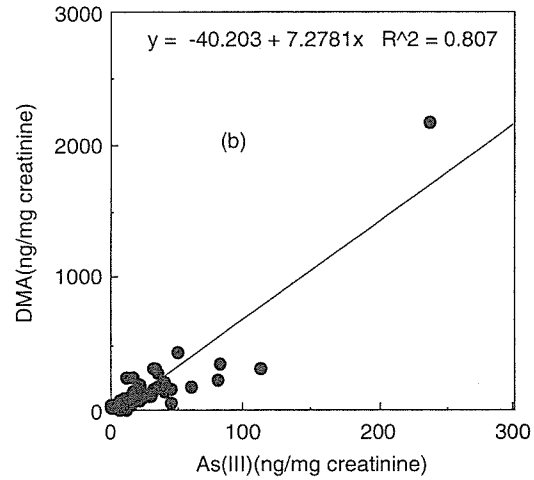
	Sample	Creatinine (mg ml^{-1})	Arsenic (ng mg^{-1} creatinine)					(MMA + DMA)/Total As (%)
			As(III)	DMA	MMA	As(V)	Total As	
2	A-1	0.236	11.9	251.8	32.0	<0.2	295.8	96.0
3	A-2	0.443	<0.2	31.1	5.4	<0.2	36.5	100.0
4	A-3	0.956	2.7	26.6	5.9	<0.2	35.2	92.3
5	A-4	1.456	12.4	65.8	8.0	<0.2	86.2	85.6
6	B-1	1.413	2.1	31.2	13.7	<0.2	47.1	95.4
7	B-2	0.279	1.7	29.7	17.7	<0.2	49.0	96.6
8	C-1	0.421	7.3	72.6	14.5	<0.2	94.4	92.3
9	C-2	0.625	21.5	203.7	14.7	<0.2	239.9	91.0
10	C-3	0.120	1.2	19.8	<0.2	<0.2	21.0	94.4
11	D-1	0.873	15.4	100.6	2.0	<0.2	118.1	86.9
12	D-2	0.540	26.6	115.0	<0.2	0.4	142.0	81.0
13	D-3	0.894	35.1	289.0	<0.2	19.3	343.4	84.2
14	D-4	0.277	11.7	92.0	<0.2	<0.2	103.7	88.7
15	E-1	0.958	15.6	249.5	14.5	<0.2	279.6	94.4
16	F-1	0.475	44.8	157.4	12.9	<0.2	215.1	79.2
17	F-2	0.471	32.3	159.9	15.4	<0.2	207.7	84.4
18	F-3	0.855	112.5	325.8	15.8	1.3	455.5	75.0
19	F-4	0.696	41.3	150.7	18.8	<0.2	210.7	80.4
20	F-5	0.294	16.9	140.9	11.1	3.4	172.4	88.2
21	F-6	1.077	49.7	438.0	48.6	1.1	537.4	90.5
22	F-7	0.577	29.3	105.8	9.1	<0.2	145.1	79.2
23	G-1	0.817	20.3	102.5	20.5	<0.2	143.2	85.9
24	G-2	0.070	3.1	18.6	<0.2	<0.2	21.8	85.6
25	G-3	0.277	9.5	49.3	14.8	<0.2	73.7	87.1
26	G-4	0.279	8.2	47.9	12.4	<0.2	68.5	88.0
27	G-5	0.086	6.3	14.2	<0.2	<0.2	20.5	69.2
28	G-6	0.403	14.4	34.3	6.8	<0.2	55.5	74.1
29	H-1	0.804	32.3	322.6	40.0	5.3	400.3	90.6
30	I-1	0.173	0.6	18.6	1.6	<0.2	20.8	97.3
31	I-2	0.598	4.1	28.5	8.8	<0.2	41.4	90.0
32	I-3	1.290	59.4	170.6	34.9	<0.2	264.9	77.6
33	I-4	0.201	5.1	27.7	1.3	<0.2	34.1	85.1
34	I-5	0.995	7.6	23.5	3.6	<0.2	34.7	78.2
35	J-1	0.362	45.0	64.2	25.5	11.9	146.6	61.2
36	J-4	0.308	21.4	71.3	<0.2	<0.2	92.7	76.9
37	K-1	0.803	237.4	2166.4	430.6	55.5	2890.0	89.9
38	K-2	0.154	79.2	220.1	73.0	5.6	377.8	77.6
39	L-1	0.470	36.0	171.6	41.9	<0.2	249.4	85.6
40	L-2	0.484	29.2	113.2	22.7	<0.2	165.0	82.3
41	L-3	1.160	11.8	0.0	8.9	89.7	110.4	8.0
42	M-1	0.319	10.1	82.9	13.7	<0.2	106.8	90.6
43	M-2	0.213	7.6	62.4	9.3	<0.2	79.3	90.5
44	M-3	1.319	81.6	342.6	52.7	3.2	480.1	82.3
45	M-4	0.425	40.4	210.5	17.7	4.6	273.2	83.5
	Average	0.590	28.7	168.6	25.0	4.6	227.0	83.9
	Max.	1.456	237.4	2166.4	430.6	89.7	2890.0	100.0
	Min.	0.070	<0.2	<0.2	<0.2	<0.2	20.5	8.0

was 408.4 ppb. On comparing the urinary total arsenic of K-2 (377.8 ng mg^{-1} creatinine) with that of K-1 (2890.0 ng mg^{-1} creatinine), we can conclude that K-1 must recently have taken the arsenic-contaminated water from the shallow tubewell-water instead of the deep tubewell-water.

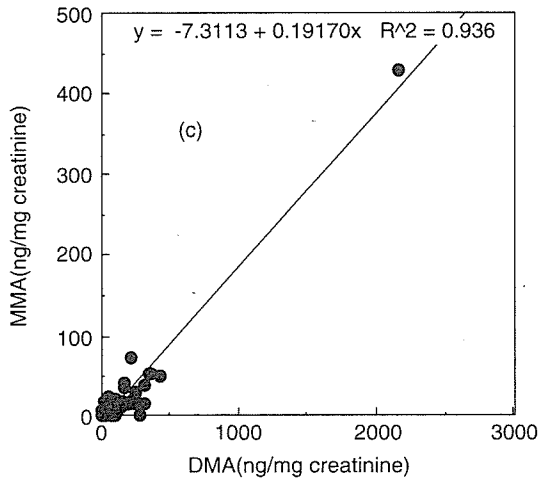
We have already reported in our earlier publications[12,13] that the average of urinary arsenic(III), DMA, MMA and arsenic(V) in the Jalangi block were 92.0 ng mg^{-1}, 391.4 ng mg^{-1}, 62.1 ng mg^{-1} and 45.4 ng mg^{-1} creatinine respectively. And those in the Domkal block were 24.5 ng ml^{-1}, 136.1 ng ml^{-1}, 25.5 ng ml^{-1} and 58.3 ng ml^{-1} urine respectively. The arsenic concentrations in the six shallow tubewell-water samples in the Jalangi block and in the eight tubewell-water samples in the Domkal block ranged from 7.3 to 170.0 ppb and from 0.64 to 75.5 ppb respectively. When compared with the Jalangi and Domkal populations, the population studied in Makrampur village, Beldanga block, consumed groundwaters with a lower concentration of arsenic through their deep tubewell waters. This must be reflected in the lower concentrations of arsenic species than those from the subjects of our previous studies. Vahter[18] reviewed the urinary arsenic species obtained from areas with arsenic-affected underground water, such as Taiwan, California, Santa Ana (Mexico), Toconao and San Antonio, and reported that the urinary inorganic arsenic to total arsenic ranged from 10 to 30%, MMA ranged from 10 to 20%, and DMA ranged from 60 to 70%. Also, Hsueh *et al.*[19] estimated the urinary arsenic species from previous cumulative exposure to arsenic through consuming artesian well water among healthy residents in an arseniasis hyperendemic area in Taiwan. They reported that, in the case of cumulative exposure to arsenic exceeding 10 mg l^{-1} $year^{-1}$, the average percentage (plus/minus the standard error) of (arsenic(III) + arsenic(V)), of MMA and of DMA to total arsenic in urine amples



Relationship beteen As(III) and MMA in urines



Relationship between As(III) and DMA in urines



Relationship between DMA and MMA in urines

Figure 2. Relationship between urinary As species.

was 10.27% (±0.60%, $n = 148$), 23.21% (±1.12%, $n = 148$), and 66.50% (±1.39%, $n = 148$) respectively. In our current data, shown in Table 4, the average (plus/minus the residual standard deviation) of the ratio of (MMA + DMA) to total arsenic was 86.7% (±9.2%), with the exception of the data for the L-3 urine sample. Our data are similar to the ratio of (MMA + DMA) to total arsenic obtained by Hsueh *et al.*[19] and Vahter.[18] The exception (L-3 in Table 4) was an 18-year-old boy who had a markedly low ratio of (MMA + DMA) to total arsenic (8.0%). The amount of total arsenic in his urine sample was 110.4 ng mg^{-1} creatinine and most of the arsenic species was arsenic(V), at 89.7 ng mg^{-1} creatinine. It may be speculated that the boy has a low methylating capacity of inorganic arsenic in the liver. We could not observe any arsenic symptoms from this boy, as shown in Table 2.

We estimated the relationships between each arsenic species, except for the data obtained from the boy identified as L-3. As shown in Figure 2, there were significantly positive correlations between the concentrations of arsenic(III) and MMA, arsenic(III) and DMA, and MMA and DMA ($p = 0.01$). We have already reported similar observations in our earlier publications.[12,13] The presence of these positive correlations does not contradict the postulation that the metabolic pathway of inorganic arsenic follows as arsenic(V) → arsenic(III) → MMA → DMA in the case of humans.

CONCLUSIONS

Based on the results from our field surveys of tubewell-water samples and human urine samples obtained from the Makrampur village, in the Beldanga block of the Murshidad district, we obtained the following findings.

(1) The arsenic concentrations in five shallow tubewell-water samples ranged from 18.0 to 408.4 ppb. The arsenic concentrations in four deep tubewell-water samples ranged from 5.2 to 9.6 ppb.
(2) We found 22 arsenic-affected villagers out of 44 villagers, belonging to 13 families.
(3) The concentrations of arsenic(III), DMA, MMA and arsenic(V) in urine samples obtained from the 44 villagers ranged from <0.2 to 237.4 ng mg^{-1}, <0.2 to 2166.4 ng mg^{-1}, <0.2 to 403.6 ng mg^{-1} and < 0.2 to 89.7 ng mg^{-1} creatinine respectively, and the averages were 28.7 ng mg^{-1}, 168.6 ng mg^{-1}, 25.0 ng mg^{-1} and 4.6 ng mg^{-1} creatinine respectively. The average of total arsenic was 227.0 ng mg^{-1} creatinine.
(4) One boy had a low arsenic-methylating capacity and directly excreted 81.2% of arsenic(V) against the total arsenic in his urine. One woman excreted the highest amount of total arsenic at 2890.0 ng mg^{-1} creatinine in her urine.
(5) When estimating the arsenic species in 43 urine samples obtained from families A to M, the correlations between arsenic(III) and MMA, between arsenic(III) and DMA or between MMA and DMA in urine samples were significant ($p = 0.01$).

Acknowledgements

We would like to express our sincere gratitude to Dr Chakraborti and his coworkers at the School of Environmental Studies, Jadavpur University, Kolkata, West Bengal, India. We also thank the Ministry of Environment for the financial support of the Global Environment Research Fund.

REFERENCES

1. Smith AH, Lingas EO, Rahman M. *Bull. WHO* 2000; **78**: 1093.
2. Mandal KM, Ogra Y, Suzuki KT. *Chem. Res. Toxicol.* 2001; **14**: 371.
3. Chowdhury UK, Rahman MM, Sngupta MK, Lodh D, Chanda CR, Roy S, Quarmruzzan Q, Tokunaga H, Ando M, Chakraborti D. *J. Environ. Sci. Health* 2003; **38**: 87.
4. Tseng WP, Chu HM, Fong JM, Lin CS, Yen S. *J. Natl. Cancer Inst.* 1968; **40**: 453.
5. Berg M, Tran HC, Nguyen TC, Pham HV, Schertenkeib R, Giger W. *Environ. Sci. Technol.* 2001; **35**: 2621.
6. Christen K. *Environ. Sci. Technol.* 2001; **35**: 286A.
7. Chakraborti AK, Saha KC. *Indian J. Med. Res.* 1987; **85**: 326.
8. Chowdhury T, Basu GK, Mandal BK, Biswas BK, Chowdhury UK, Chanda CR, Lodh D, Roy SL, Saha KC, Roy S, Kabir S, Quamruzzaman Q, Chakraborti D. *Nature* 1999; **401**: 545.
9. Chowdhury UK, Biswas BK, Chowdhury TR, Samanta G, Mandal BK, Basu GC, Chanda CR, Lodh D, Saha KC, Mukherjee SK, Roy S, Kabir S, Quamruzzaman Q, Chakraborti D. *Environ. Health Perspect.* 2000; **108**: 393.
10. Rahman MM, Chowdhury UK, Mukherjee SC, Mondal BK, Paul K, Lodh D, Biswas BK, Chanda CR, Basu GK, Saha KC, Roy S, Das R, Palit SK, Quamruzzaman Q, Chakraborti D. *J. Toxicol. Clin. Toxicol.* 2001; **39**: 683.
11. Rahman MM, Mukherjee D, Sengupta MK, Chowdhury UK, Lodh DC, Roy S, Selim M, Quamruzzaman Q, Milton AH, Shahidullah SM, Rahman MT, Chakraborti D. *Environ. Sci. Technol.* 2002; **36**: 5385.
12. Tokunaga H, Roychowdhury T, Chandraskaran N, Uchino T, Ando M. *Appl. Organometal. Chem.* 2002; **16**: 406.
13. Tokunaga H, Roychowdhury T, Uchino T, Ando M. *J. Health Sci.* 2003; **49**: 464.
14. Roychowdhury T, Uchino T, Tokunaga H, Ando M. *Sci. Total Environ.* 2003; **308**: 15.
15. Dhar RK, Biswas BK, Samanta G, Mandal BK, Chakraborti D, Roy S, Jafar A, Islam A, Ara G, Kabir S, Khan AW, Ahmed SK, Hadi SA. *Curr. Sci.* 1997; **74**: 134.
16. Biswas BK, Dhar RK, Samanta G, Mandal BK, Chakraborti D, Faruk I, Islam KS, Chowdhury MM, Islam A, Shitosh R. *Curr. Sci.* 1997; **73**: 48.
17. Calderson RL, Hudgens E, Le XC, Schreinemachers D, Thomas DJ. *Environ. Health Perspect.* 1999; **107**: 663.
18. Vahter M. *Arch. Toxicol. Lett.* 2000; **112–113**: 209.
19. Hsueh YM, Ko YF, Huag YK, Chen HW, Chiou HY, Huang YL, Yang MH, Chem CJ. *Toxicol. Lett.* 2003; **137**: 49.

ELSEVIER

Chemosphere 58 (2005) 799–810

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Effect of arsenic-contaminated irrigation water on agricultural land soil and plants in West Bengal, India

Tarit Roychowdhury *, Hiroshi Tokunaga, Tadashi Uchino, Masanori Ando

Division of Environmental Chemistry and Exposure Assessment, National Institute of Health Sciences, 1-18-1 Kamiyoga, Setagaya Ku, Tokyo 158-8501, Japan

Received 6 January 2004; received in revised form 24 August 2004; accepted 31 August 2004

Abstract

Total arsenic withdrawn by the four shallow tubewells, used for agricultural irrigation in the arsenic-affected areas of Murshidabad district per year is 6.79 kg (mean: 1.79 kg, range: 0.56–3.53 kg) and the mean arsenic deposition on land per year is 5.02 kg ha^{-1} (range: 2–9.81 kg ha^{-1}). Mean soil arsenic concentrations in surface, root of plants, below ground level (0–30 cm) and all the soils, collected from four agricultural lands are 14.2 mg/kg (range: 9.5–19.4 mg/kg, $n = 99$), 13.7 mg/kg (range: 7.56–20.7 mg/kg, $n = 99$), 14.8 mg/kg (range: 8.69–21 mg/kg, $n = 102$) and 14.2 mg/kg (range: 7.56–21 mg/kg, $n = 300$) respectively. Higher the arsenic in groundwater, higher the arsenic in agricultural land soil and plants has been observed. Mean arsenic concentrations in root, stem, leaf and all parts of plants are 996 ng/g (range: <0.04–4850 ng/g, $n = 99$), 297 ng/g (range: <0.04–2900 ng/g, $n = 99$), 246 ng/g (range: <0.04–1600 ng/g, $n = 99$) and 513 ng/g (range: <0.04–4850 ng/g, $n = 297$) respectively. Approximately 3.1–13.1, 0.54–4.08 and 0.36–3.45% of arsenic is taken up by the root, stem and leaf respectively, from the soil.

Keywords: Agricultural irrigation; Groundwater; Soil and plant; Microwave digestion; ICP-MS; Arsenic

1. Introduction

Natural groundwater arsenic-contamination and sufferings of people have become a crucial water quality problem in many parts of the world, particularly in Bengal Delta, Bangladesh and West Bengal, India (Chowdhury et al., 2000, 2001). More than 100 million people are living in the arsenic-affected districts of these two countries. In the nine arsenic-affected districts, out of total 18 districts in West Bengal, 74 blocks and approximately 2700 villages have been identified where groundwater contains arsenic above 0.05 mg/l (Chakraborti et al., 2002). Groundwater is the main source for drinking, cooking and other household purposes in these arsenic-affected districts. Even the agricultural system is mostly groundwater dependent. Forty to 45 years earlier, agriculture in West Bengal was rain dependent and in each year there was only one crop following the monsoon. But at present, to meet the food demands of the increasing population, the growing season has been expanded from one to four or five crops per year. Rainwater alone can no longer meet the water demand of such intensive agriculture, since only limited rainfall occurs during the dry season. Therefore, agriculture has

* Corresponding author. Tel.: +81 3 3700 1141x318; fax: +81 3 3707 6950.

E-mail addresses: tarit@nihs.go.jp, rctarit@yahoo.com (T. Roychowdhury).

0045-6535/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2004.08.098

shifted to using groundwater to supplement the rainwater supplies. For this purpose, thousands of shallow large-diameter tubewells were installed for agricultural irrigation. Many millions of cubic meters of groundwater contaminated with arsenic and other heavy metals are used for agricultural irrigation and are deposited in the soil throughout the year. As a result, groundwater exploitation goes on unchecked. The status of aquifer exploitation is as high as 79.40% from a single district, North 24-Parganas (Directorate of Agricultural Engineering, 1991). More than 95% of the Rural Water Supply Schemes (RWSS) in West Bengal are dependent on groundwater. In Deganga, one of the severely arsenic-affected blocks in West Bengal, 38% of the shallow tubewells ($n = 597$), used for agricultural irrigation contain arsenic above 0.05 mg/l (average = 0.133 mg/l) and 96% shallow tubewells ($n = 574$) contain arsenic above 0.01 mg/l (average = 0.07 mg/l, range: 0.01–0.84 mg/l) (Mandal, 1998). A single Rural Water Supply Scheme (RWSS) (Mothabari, Kaliachalk-II) in one of the affected districts (Malda) of West Bengal is alone withdrawing 147 kg of arsenic from groundwater in a year (Mandal et al., 1996). About 6.4 tons and 0.176 tons of arsenic are coming out per year from all the shallow tubewells ($n = 3072$), used for agricultural irrigation and hand tubewells ($n = 9190$), used for drinking, cooking and other household purposes by the villagers in Deganga block, North 24-Parganas district (Mandal, 1998). Moreover, possibility of soil contamination could not be ignored (Roychowdhury et al., 2002b). Crops grown on these soils are expected a major unrecognized route for arsenic exposure (Roychowdhury et al., 2002a; Meharg and Rahman, 2003).

The absorption of arsenic by plants is influenced by the concentration of arsenic in soil (National Research Council, 1977). The relationships between the amount of arsenic in soil, plant growth and arsenic toxicity have been investigated (Schoenhard and Koenig, 1975; Walsh et al., 1977). The relationships between soil arsenic and growth of plants depend on the form and availability of the arsenic. The toxicity of arsenic varies with its form and valence, its toxic order being AsH_3 > As(III) > As(V) > organic As (Wu and Xie, 1990). In general, arsenic availability to plants is highest in coarse-textured soils having little colloidal material and little ion exchange capacity, and lowest in fine-textured soils high in clay, organic material, iron, calcium and phosphate (National Research Council of Canada, 1978). To be absorbed by plants, arsenic compounds must be in a mobile form in the soil solution. Except for locations where arsenic content is high (e.g. around smelters), the accumulated arsenic is distributed throughout the plant body in nontoxic amounts (National Research Council, 1977).

The present study is centered on Hariharpara and Raninagar-II blocks of Murshidabad district. Murshidabad is one of the nine arsenic-affected districts in West Bengal, India where groundwater contains arsenic above 0.05 mg/l, the maximum permissible limit recommended by WHO (Chowdhury et al., 2000; Chakraborti et al., 2002). The district forms a part of the deltaic alluvial plain of the modern Ganga–Brahmaputra delta and is underlain by fluviatile sediments of Quaternary age. The arsenic content in groundwater in 19, out of a total of 26 blocks in Murshidabad exceeds the 0.05 mg/l limit and in 22 blocks above 0.01 mg/l limit. About 66% and 32% of the analyzed tubewell water samples ($n = 22274$) in the 19 arsenic-affected blocks of Murshidabad district contain arsenic above 0.01 and 0.05 mg/l respectively (Chakraborti et al., 2002). Hariharpara and Raninagar-II are two severely arsenic-affected blocks, out of a total of 19 blocks in Murshidabad district where people with arsenical skin lesions have been reported (Mandal et al., 1999). The area and population of Hariharpara and Raninagar-II blocks are 252 km^2, 195 km^2 and 185 538, 132 677 respectively (according to 1991 census). The agricultural system in this area is mostly groundwater dependent. Except the rainy reason (July–October), the agricultural land soils have been exposed to irrigated groundwater round the year. Even, sometimes the farmers used to run the shallow tubewells in the rainy season due to insufficient rain. Most of the vegetables and other foodstuffs, used by the villagers were cultivated in this area and entered the local market. Those who have individual agricultural land used to collect the foodstuffs from their own plots. The main objective of this study is to locate the magnitude of soil contamination, followed by plant contamination by arsenic due to huge withdrawal of groundwater in this area.

2. Materials and methods

2.1. Sample collection and preparation

The demography of West Bengal was described elsewhere (Roychowdhury et al., 2002b). Water, soil and plant samples were collected from the two gram-panchayets (g.p), out of a total of 10, from Hariharpara block and from two gram-panchayets, out of a total of 9, from Raninagar-II block in the Murshidabad district during December, 2001. The gram-panchayets are Khidirpur and Hariharpara in Hariharpara block and Malibari-I and Rajapur in Raninagar-II block. We selected those severely arsenic-affected locations for collection of samples where people were suffering with arsenical skin lesions.

Water samples were collected from the shallow, large-diameter tubewells, used for agricultural irrigation. The water samples were not filtered during collection or prior to analysis, stored in polyethylene bottles,

which were pre-washed with concentrated nitric acid (1:1) and nitric acid (0.1% v/v) was added as preservative (Chatterjee et al., 1993). The analyses of water samples represented the total load of arsenic (dissolved plus colloid-bound) in the water samples.

Agricultural land soils (~20–25 g) were collected from the (a) upper surface of the land (with a Teflon knife after scraping away the top 0.5 cm and up to a depth of maximum 5 cm from the upper surface), (b) root after pick off the plants, cultivated on the agricultural lands and (c) below ground level (up to a depth of 30 cm and at every 5 cm interval from the upper surface). The soil samples were mainly clay in nature.

Soil samples were collected from four agricultural lands (mean area: 0.32 ha, range: 0.28–0.36 ha). Each agricultural land consisted of many sub-lands having various cultivated plants. The plants cultivated in the sub-lands, during our field survey were cabbage, cauliflower, gram, garlic, radish, lentil, wheat, mustard, egg plant and onion (village: Baruipara, g.p: Khidirpur), cabbage, cauliflower, garlic, lentil, wheat, mustard, onion, potato and coriander (village: Komnagar, g.p: Hariharpara), lentil, mustard, radish, tomato, egg plant and spinach (village: Rakhaldaspur, g.p: Malibari-I) and wheat, mustard, tomato, peas, radish, garlic, potato and beans (village: Dobopara, g.p: Rajapur). Other than these crops, the farmers used to cultivate paddy, gourd, pumpkin, papaya, bitter gourd and other edible herbs throughout the year. The surface soils were collected from each sub-land (each sample consisted of three sub-samples having a distance of approximately 600 cm between each other). The soils from the root (each sample consisted of three sub-samples having a distance of approximately 300 cm between each other) were collected mainly from these plants, cultivated in each sub-land. The cleaning (removal of soil) of samples was performed by shaking and sometimes by using a dry pre-cleaned vinyl brush (Queirolo et al., 2000). The soils below ground level were collected from the three spots of each of individual field (mustard, garlic and arum) in Baruipara village, two spots of each of the individual field (mustard, garlic and arum) in Rakhaldaspur village and two spots of mustard field in Dobopara village. The soils below ground level were not collected from the agricultural land in Komnagar village. The spots were approximately 300 cm apart between each other in the same field. The agricultural land soils have been exposed to irrigation water. The shallow, large-diameter tubewells were used for agricultural irrigation (running 7 h a day and 7 months per year). The shallow tubewells were with 7–10 cm in diameter and about 20 m^3/h discharge rate. They run with the help of electric/diesel pump (average 5 HP). The irrigation water from the source reaches to the plants through mainly small canals in the fields or sometimes through plastic pipes or rarely operated by manually. Except the rainy season (June–October), the shallow tubewells run throughout the year. Even sometimes the farmers used to run the shallow tubewells in the rainy season due to insufficient rain. The irrigation also depends on the water requirements for the crops and vegetables, cultivated in these areas. Other than the irrigation water, the soils have been exposed to rainwater throughout the year, especially in rainy season or sometimes have been exposed to flooded river or pond water during the heavy rain in rainy season.

Soil samples were placed in individual polyethylene bags and transported to our laboratory by air. The samples were dried in open air under diffused sunlight followed by drying in an oven at 50 °C for 24 h, manually ground to a fine powder with a mortar and passed through a 30-mesh sieve (Chatterjee et al., 1993; Roychowdhury, 1999; Chakraborti et al., 2001).

The plants (each sample consisted of three sub-samples having a distance of approximately 300 cm between each other) were approximately 30–35 days old. The plants from all the four agricultural lands were sampled by hands protected with vinyl gloves, carefully placed in individual polyethylene bags, stored in a cold box at 4 °C and transported to our laboratory by air (Queirolo et al., 2000). All the plants were kept at 4 °C until further treatment. After keeping at room temperature for several hours, the root, stem and leaf parts of each plant were separated with a quartz knife. At first, all the parts (special attention was made on root to remove the soil) were washed manually by tap water and finally by deionized water (Queirolo et al., 2000) in an ultrasonic cleaner (50/60 Hz, Model No. B-220; Branson, USA). All the parts were dried in open air under diffused sunlight for 24 h, followed by drying in an oven at 50 °C for complete dryness, manually ground to a fine powder (homogenized) with a mortar and passed through a 30-mesh sieve.

2.2. Chemicals and reagents

All reagents were of analytical grade. MilliQ water (Yamato Millipore-filter, WT 100) was used throughout. Stock solution of arsenic (arsenic trioxide) with concentration of 1000 mg/l (Cica-Reagent, Chuo-Ku, Tokyo, Japan) was used for the standard solution preparation of ICP-MS. The sample digestions were carried out with concentrated nitric acid and high purity hydrogen peroxide (30–35.5%) from Wako Pure Chemical Industries Ltd., Osaka, Japan. Details of the reagents and Standard Reference Materials were described elsewhere (Roychowdhury et al., 2002a,b).

2.3. Digestion

A microwave digestion system (MARS 5) from CEM Corporation, Matthews, North Carolina 28106, USA

with a rotor for 14 Teflon digestion vessels HP-500, was used for sample digestion. Details of the digestion procedures and microwave condition for digestion were described elsewhere (Roychowdhury et al., 2002a,b).

2.4. Analysis

An inductively coupled plasma mass spectrophotometer (ICP-MS; Hewlett-Packard 4500) was used as a chromatographic detector. The ICP-MS system was equipped with a Shimadzu LC-10ADVP liquid chromatograph solvent delivery pump and a Shimadzu DGU-12A degasser and a double-pass, Scott-type spray chamber (water cooled, 2 °C) (ORION, RKS-1500V-C). The instrumental conditions were described elsewhere (Roychowdhury et al., 2002a). The detection limit of arsenic in our system is 0.04 μg/l. Off-line data from the ICP-MS were processed with special chromatographic software (HP ChemStation).

3. Results

Arsenic withdrawn and deposition on agricultural land per year by each of the four shallow tubewells in the surveyed areas, used for agricultural irrigation is shown in Table 1. The total arsenic withdrawn by these four shallow tubewells per year is 6.79 kg (mean: 1.79 kg, range: 0.56–3.53 kg) and the mean arsenic deposition per land by the shallow tubewells per year is 5.02 kg ha^{-1} (range: 2–9.81 kg ha^{-1}). Arsenic levels in agricultural land soils are shown in Table 2. The mean arsenic concentrations in surface soils, soils from the root of plants, soils below ground level (0–30 cm) (17 spots from seven sub-lands in three agricultural lands) and all soils from the four agricultural lands are 14.2 mg/kg (range: 9.5–19.4 mg/kg, $n = 99$), 13.7 mg/kg (range: 7.56–20.7 mg/kg, $n = 99$), 14.8 mg/kg (range: 8.69–21 mg/kg, $n = 102$) and 14.2 mg/kg (range: 7.56–21 mg/kg, $n = 300$) respectively. Distribution of arsenic concentration in soil with increasing depth is shown in Fig. 1. The mean arsenic concentrations in soils below ground level (up to a depth of 30 cm and at every 5 cm interval from the upper surface) from the three spots of each of mustard, garlic and arum sub-land in Baruipara agricultural land are 15.3 mg/kg (range: 12.1–17.5 mg/kg, $n = 18$), 17.5 mg/kg (range: 12.2–21 mg/kg, $n = 18$) and 15.3 mg/kg (range: 11.4–19.8 mg/kg, $n = 18$) respectively. Similarly, the mean arsenic concentrations in soils below ground level from the two spots of each of mustard, garlic and arum sub-land in Rakhaldaspur agricultural land are 14.3 mg/kg (range: 12.8–16 mg/kg, $n = 12$), 14.2 mg/kg (range: 9.38–19.8 mg/kg, $n = 12$) and 15.5 mg/kg (range: 12.1–17.9 mg/kg, $n = 12$) respectively. The mean arsenic concentration in soils below ground level from the two spots of mustard field in Dobopara agricultural land is 10 mg/kg (range: 8.69–11.9 mg/kg, $n = 12$). The mean arsenic concentrations in soils below ground level from the total nine spots of three fields in Baruipara agricultural land and six spots of three fields in Rakhaldaspur agricultural land are 16.0 mg/kg (range: 11.4–21 mg/kg, $n = 54$) and 14.6 mg/kg (range: 9.38–19.8 mg/kg, $n = 36$) respectively. The soil arsenic concentration increases with increase of water arsenic concentration in the surveyed area

Table 1
Arsenic withdrawn and deposition on agricultural land by each of the shallow tubewell in Hariharpara and Raninagar-II blocks, Murshidabad district

Location	Agricultural field	Land area (ha)	As in shallow water (mg/l)	Discharge rate of water[a] (m^3/h)	Arsenic withdrawn by each well per year[b](kg)	Arsenic deposition per land by each well per year (kg ha^{-1})
Vill: Baruipara, GP: Khidirpur, Block: Hariharpara	AF 1	0.36	0.12	20	3.53	9.81
Vill: Komnagar, GP: Hariharpara, Block: Hariharpara	AF 2	0.32	0.029	20	0.85	2.66
Vill: Rakhaldaspur, GP: Malibari-I, Block: Raninagar-II	AF 3	0.33	0.063	20	1.85	5.62
Vill: Dobopara, GP: Rajapur, Block: Raninagar-II	AF 4	0.28	0.019	20	0.56	2

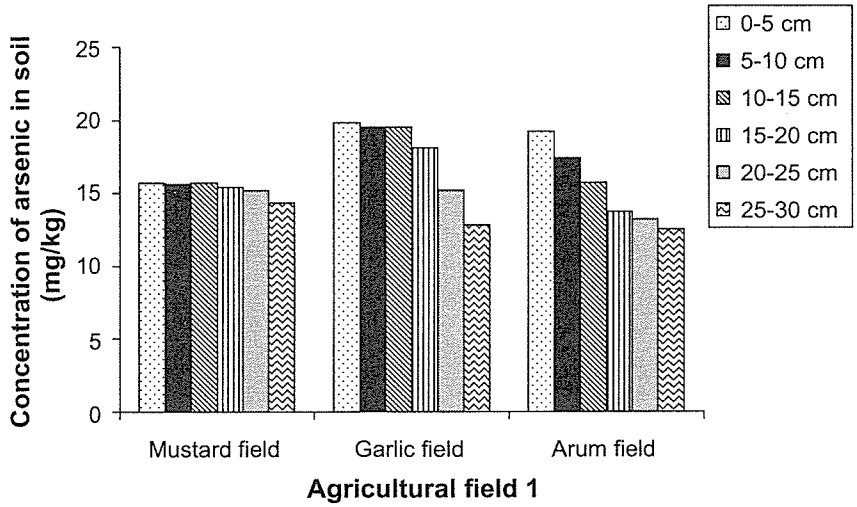
[a] Discharge rate of water = 20 m^3/h = 20 × 7 m^3/day (average 7 h per day each well runs) = 20 × 7 × 210 m^3/year (about 7 months per year each runs) = 20 × 7 × 210 × 1000 l/year (1 m^3 = 1000 l) = 2.94 × 10^7 l/year.

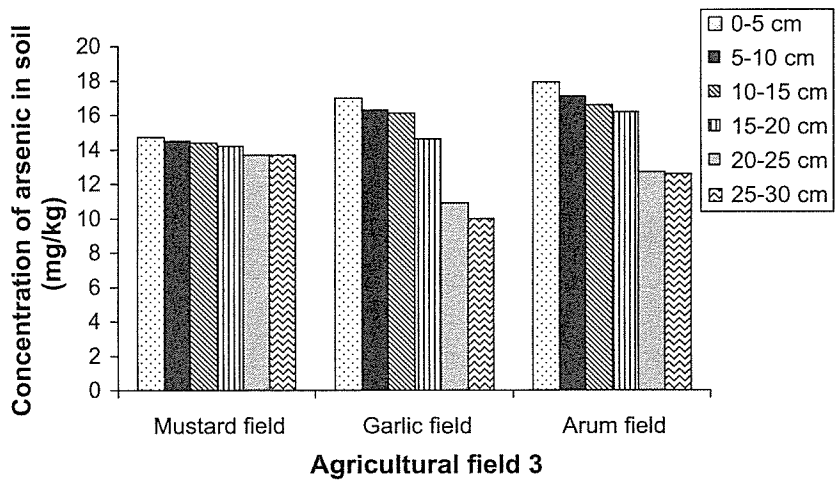
[b] Arsenic withdrawn by each well per year = Discharge rate of water[a] × Arsenic in each shallow tubewell water.

Table 2
Arsenic levels (mg/kg) in agricultural land soils from Hariharpara and Raninagar-II blocks, Murshidabad district

Location	Agricultural field	No. of sub-lands	Arsenic in soil											
			Surface soil[a]			Soil from the root of plants[a]			Soil below ground level (0–30 cm)			All soils		
			n	Mean	Range	*n*	Mean	Range	*n*	Mean	Range	*n*	Mean	Range
Vill: Baruipara, GP: Khidirpur, Block: Hariharpara	AF 1	10	30	17.6	15.8–19.4	30	18.3	15.9–20.7	54	16.0	11.3–21	114	16.4	11.3–21
Vill: Komnagar, GP: Hariharpara, Block: Hariharpara	AF 2	9	27	13.2	10.0–14.3	27	11.4	8.32–14.6	NC	NC	NC	54	12.6	8.32–14.6
Vill: Rakhaldaspur, GP: Malibari-I, Block: Raninagar-II	AF 3	6	18	15.9	14.2–17.9	18	14.7	12.0–18.4	36	14.6	9.38–19.8	72	14.8	9.38–19.8
Vill: Dobopara, GP: Rajapur, Block: Raninagar-II	AF 4	8	24	10.5	9.5–11.6	24	9.83	7.56–11.0	12	10.0	8.69–11.9	60	10.1	7.56–11.9

NC: not collected.
[a] Each sample consisted of three sub-samples.





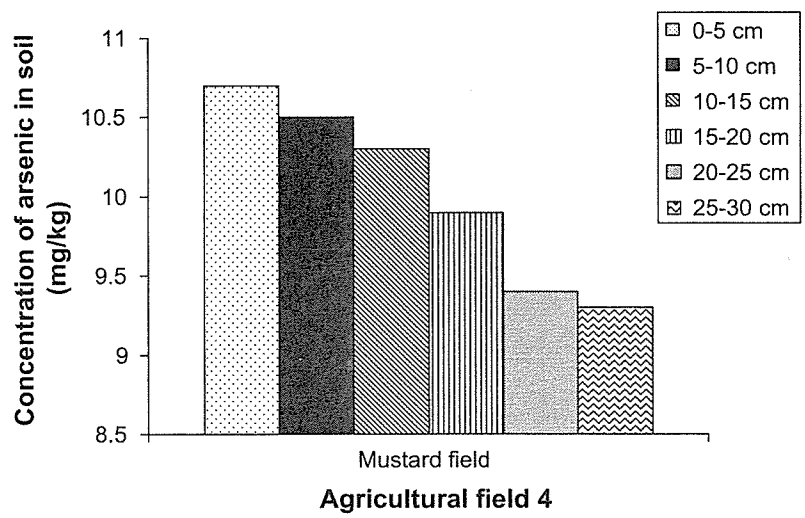


Fig. 1. Distribution of arsenic concentration in soil with increasing depth.

(Tables 1 and 2). Regression analyses have been carried out between arsenic concentration in shallow tubewell water and arsenic concentration in agricultural land soils (Fig. 2). The linear regressions show good correlation between water arsenic concentration vs surface soils ($r^2 = 0.738$, $p < 0.0001$), soils from the root of plants ($r^2 = 0.712$, $p < 0.0001$) and soils below ground level ($r^2 = 0.623$, $p < 0.0002$) respectively.

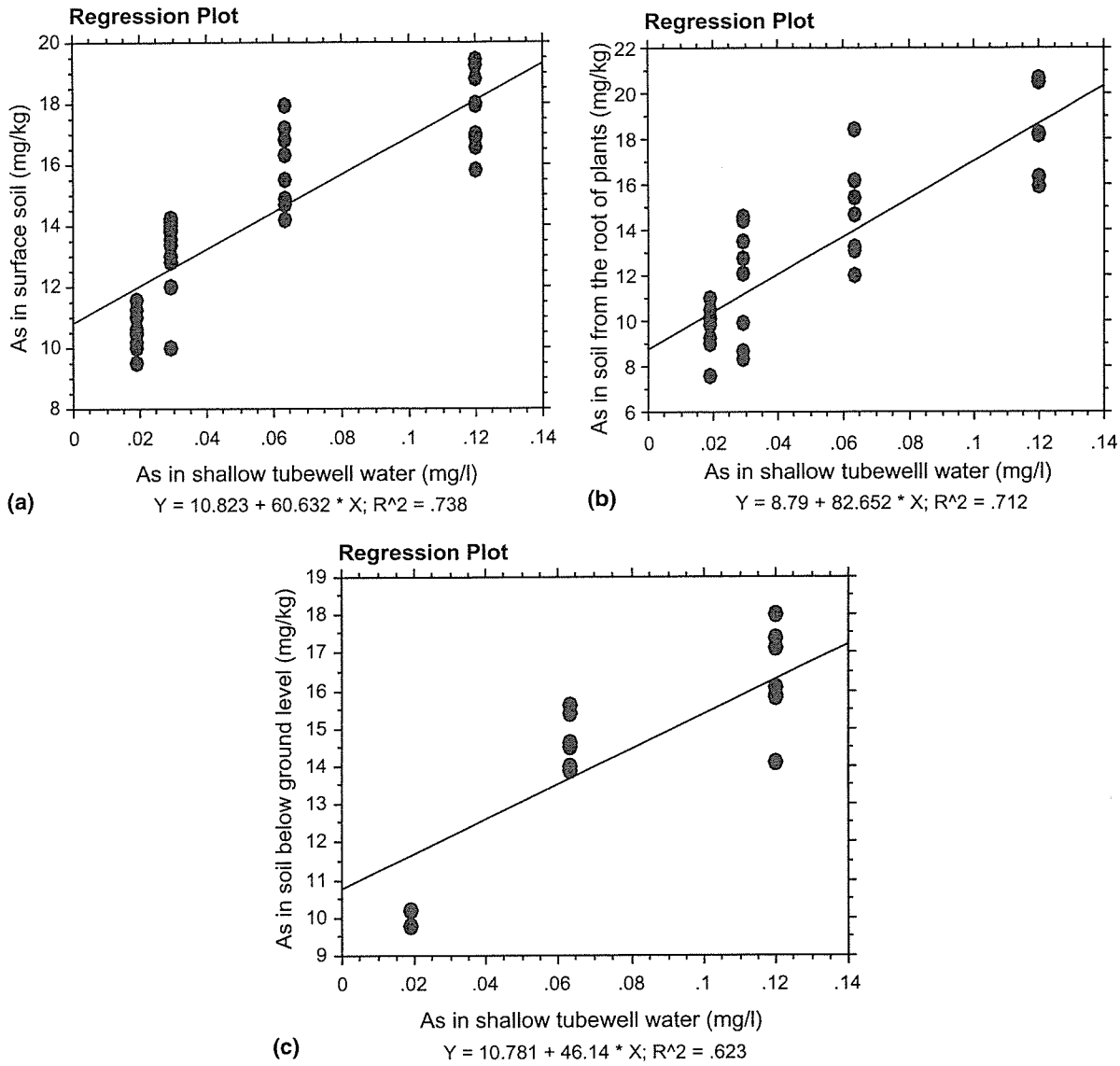


Fig. 2. Regression plot between arsenic in irrigated water vs arsenic in soil: (a) water vs surface soil, (b) water vs soil from the root and (c) water vs soil below ground level.

Arsenic levels in different parts of plants from the surveyed areas are shown in Table 3. The mean arsenic concentrations in root, stem, leaf and all parts of plants from the four agricultural lands are 996 ng/g (range: <0.04–4850 ng/g, $n = 99$), 297 ng/g (range: <0.04–2900 ng/g, $n = 99$), 246 ng/g (range: <0.04–1600 ng/g, $n = 99$) and 513 ng/g (range: <0.04–4850 ng/g, $n = 297$) respectively. Distribution of arsenic in different parts of plants with increasing arsenic concentration in irrigated water and soil are shown in Fig. 3. Regression analyses have been carried out between arsenic concentration in irrigated water and agricultural land soils vs arsenic concentration in different parts of plants. The linear regressions show direct correlation between arsenic concentration in water vs root ($r^2 = 0.972$, $p < 0.015$), soil vs root ($r^2 = 0.721$, $p < 0.15$), water vs stem ($r^2 = 0.991$, $p < 0.005$), soil vs stem ($r^2 = 0.832$, $p < 0.09$), water vs leaf ($r^2 = 0.991$, $p < 0.005$) and soil vs leaf ($r^2 = 0.828$, $p < 0.09$) respectively (Fig. 4).

4. Discussion

Arsenic is a commonly occurring toxic metal in the environment. Addition of arsenic compounds to soils may be toxic to plants directly or may accumulate in plants and enter the animal and human food chain (National Research Council, 1977). The adsorption and retention of arsenic by soils control its persistence, activity, movement, transformation, and ecological effects (Wauchope and McDowell, 1984; Luo et al., 1991). The ingestion of arsenic via locally grown vegetables

Table 3
Arsenic levels (ng/g) in different parts of plants from Hariharpara and Raninagar-II blocks, Murshidabad district

Location	Agricultural field	No. of sub-lands	Arsenic in different parts of plants[a]									
			Root			Stem			Leaf			All parts		
			n	Mean	Range	*n*	Mean	Range	*n*	Mean	Range	*n*	Mean	Range
Village: Baruipara, GP: Khidirpur, Block: Hariharpara	AF 1	10	30	2150	84–4850	30	670	<0.04–2900	30	567	44–1600	90	1129	<0.04–4850
Village: Komnagar, GP: Hariharpara, Block: Hariharpara	AF 2	9	27	391	<0.04–1380	27	67.6	<0.04–560	27	46	<0.04–223	81	168	<0.04–1380
Village: Rakhaldaspur, GP: Malibari-I, Block: Raninagar-II	AF 3	6	18	836	352–1630	18	343	<0.04–892	18	285	<0.04–870	54	488	<0.04–1630
Village: Dobopara, GP: Rajapur, Block: Raninagar-II	AF 4	8	24	353	<0.04–932	24	54.7	<0.04–420	24	38.7	<0.04–214	72	149	<0.04–932

[a] Each samples consisted of three sub-samples.

may be increased in situations where the vegetables are grown in an area with elevated atmospheric deposition and contamination of cultivated land. Past use of lead arsenate as an insecticide in apple orchards may still be a source of arsenic in vegetables grown in the contaminated soil (Kenyon et al., 1979; Aten et al., 1980). Contamination by arsenic in crop plants has been reported around secondary lead smelters (Temple et al., 1977; Larsen, 1980). Uptake of arsenic and chromium by kale, lettuce, carrots and potatoes grown near a wood preservation factory due to atmospheric deposition around point sources has also been reported (Larsen et al., 1992). A sawmill that incinerated wood impregnated with arsenic, chromium and copper was also the source of contamination by arsenic and chromium in the environment (Aggett and Aspell, 1980). Elevated arsenic levels were found in leafy vegetation sampled close to the smelters and the sawmill, while arsenic in root vegetables were at a normal level.

The situation in this study is quite different from all these other studies. In this case, arsenic-contaminated groundwater was used for agricultural irrigation. Many millions of cubic meters of groundwater along with arsenic were coming out and depositing on the soil throughout the year from the shallow tubewells, used for agricultural irrigation (Table 1). Thus, the agricultural land soils were contaminated (Table 2). Higher the arsenic in irrigated groundwater, higher the arsenic in agricultural land soil has been observed (Fig. 2). In a similar study it has been reported that the mean arsenic concentration in agricultural land surface soil from another severely arsenic-affected block Domkal, Murshidabad district was 10.7 mg/kg (range: 3.34–31.6 mg/kg, $n = 180$), which was higher than the mean arsenic concentration in fallow land soils (mean: 5.31 mg/kg, range: 2.68–6.79 mg/kg, $n = 172$) in that area (Roychowdhury et al., 2002b). The mean arsenic concentration in shallow tubewells, used for agricultural irrigation in that area was 0.078 mg/l (range: 0.018–0.20 mg/l, $n = 19$). The agricultural system in Bangladesh throughout the year is almost similar with West Bengal, India. Survey of paddy soils throughout Bangladesh showed that arsenic levels were elevated in zones where arsenic in groundwater used for irrigation was high, and where these tubewells have been in operation for the longest period of time (Meharg and Rahman, 2003). Arsenic levels reached 46 mg/kg dry weight in the most affected zone, compared to levels below 10 mg/kg in areas with low levels of arsenic in the groundwater. These values agree our study results. The agricultural land soils have been exposed to irrigation water (running 7 h a day and 7 months per year), rainwater (mainly in rainy season, i.e. June–October) and sometimes to flooded river or pond water due to heavy rain in rainy season. So, there might be a variation in soil arsenic concentration round the year. It has been reported that the variation of soil

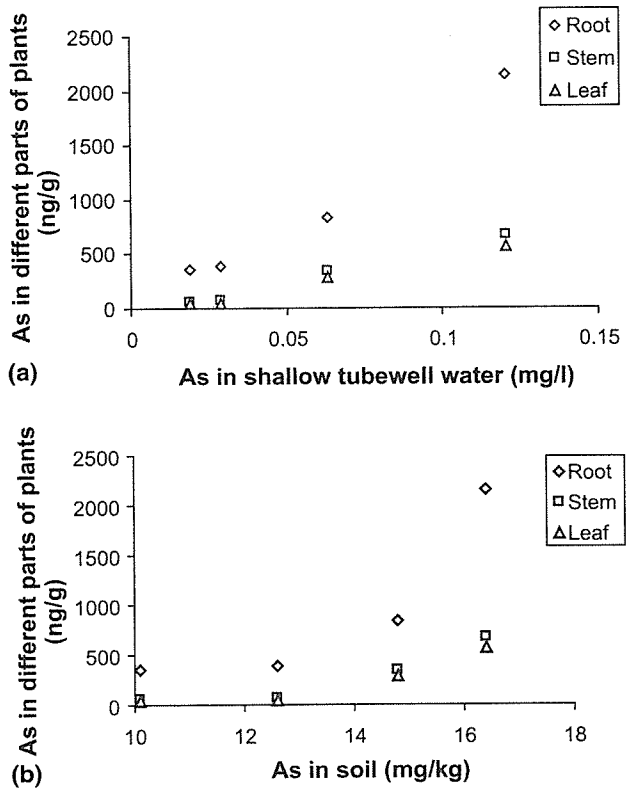


Fig. 3. Distribution of arsenic in different parts of plants with increasing arsenic concentration in (a) irrigated water and (b) soil.

arsenic concentration in 10 agricultural lands of Kolsur village, Deganga block (another severely arsenic-affected block in West Bengal) where arsenic-contaminated groundwater was used for cultivation was ±20–25% round the year (Chowdhury, 2001). The variation of soil arsenic concentrations (surface, root and below ground level) in Baruipara, Komnagar, Rakhaldaspur and Dobopara agricultural lands are ±6.82%, ±10.3%, ±4.8% and ±3.44% respectively. The variation of soil arsenic concentration below ground level (up to a depth of 30 cm and at every 5 cm interval from the upper surface) in Baruipara, Rakhaldaspur and Dobopara agricultural lands are ±11.3%, ±12.9% and ±5.8% respectively. Arsenic levels in the 0–15 cm surface paddy soils varied between 3.1 and 42.5 mg/kg (Meharg and Rahman, 2003). Arsenic levels in surface soils (0–15 cm) in the same region ranged from not detectable to 31.8 mg/kg and that arsenic levels in soil were higher in the 15–30 cm soil, with levels reaching 56 mg/kg (Alam and Sattar, 2000). Both the cases, soil arsenic levels were correlated with local well water concentrations, suggesting that the soils had become contaminated through irrigation with arsenic-contaminated water. Arsenic levels in surface soils (0–15 cm) ranged up to 83 mg/kg in another survey of Bangladesh and these soils were contaminated through irrigation with arsenic-contaminated groundwater (Ullah, 1998). In our study results, the soil arsenic concentrations are lower compared to the other studies. This is due to the fact that water arsenic concentrations in shallow tubewells used for agricultural irrigation in our study is not also so higher (Tables 1 and 2). The arsenic concentrations in surface soil, soil from the root of the plant and soil below ground level (0–30 cm), in our survey vary with different arsenic concentrations in irrigation water (Table 2, Fig. 1) and soil arsenic levels are correlated with water arsenic concentrations (Fig. 2).

A considerable amount of arsenic has been observed in different parts of plants in the study areas (Table 3). In another study, high concentration of arsenic (dry weight) has been reported in branch (2.8–14.3 mg/kg), leaf (2.1–9.5 mg/kg), trunk (0.3–55 mg/kg) and root (45–130 mg/kg) of the plants, grown up in an arsenic-contaminated soil (Jenkins, 1980). Therefore some amount of arsenic could be expected in the food chain from crops cultivated in the study areas. It has been reported that the mean arsenic levels in food categories, collected from the families living in the arsenic-affected areas of Domkal block, Murshidabad district and cultivated in that area by using arsenic-contaminated groundwater (mean: 0.085 mg/l, range: 0.018–0.20 mg/l, $n = 6$) were vegetables (123.22 ng/g, $n = 77$), cereals and bakery goods (294.47 ng/g, $n = 51$) and spices (207.6 ng/g, $n = 25$) respectively (Roychowdhury et al., 2002a). The shallow tubewells used for agricultural irrigation in the villages Komnagar and Dobopara contained less amount of arsenic (0.029 and 0.019 mg/l respectively). But we have observed an appreciable amount of arsenic in different parts of plants, collected from these two agricultural lands (Table 3) and this amount of arsenic might be able to contaminate the crops cultivated in these areas. It has been reported that only 0.018 mg/l of arsenic in the shallow tubewell water of Bakshipur agricultural land, Domkal block contaminated the food chain from crops cultivated in that area and the arsenic concentrations in foodstuffs were rice (183 ng/g), wheat flour, coarse (80 ng/g), turmeric powder (334.67 ng/g), five spices (247 ng/g), beans (200 ng/g) and green chili (130 ng/g) (Roychowdhury et al., 2002a). The individual vegetables grown in Samta village, Jassore district, Bangladesh (one of the severely arsenic-affected villages of Bangladesh) using the arsenic-contaminated irrigation water, contained the highest mean arsenic concentrations (ng/g) were snake gourd (489), ghotkol (446), taro (440), green papaya (389), elephant foot (338) and bottle ground leaf (306) respectively (Alam, 2003). The arsenic concentrations in the rice grain samples, cultivated in highly arsenic-contaminated soils of Bangladesh were reported above 1.7 mg/kg (Meharg and Rahman, 2003). Higher the arsenic in irrigated groundwater and soil, higher the arsenic in different parts of plants has been observed in our study (Figs. 3 and 4). For all the cases, the mean arsenic concentration is in

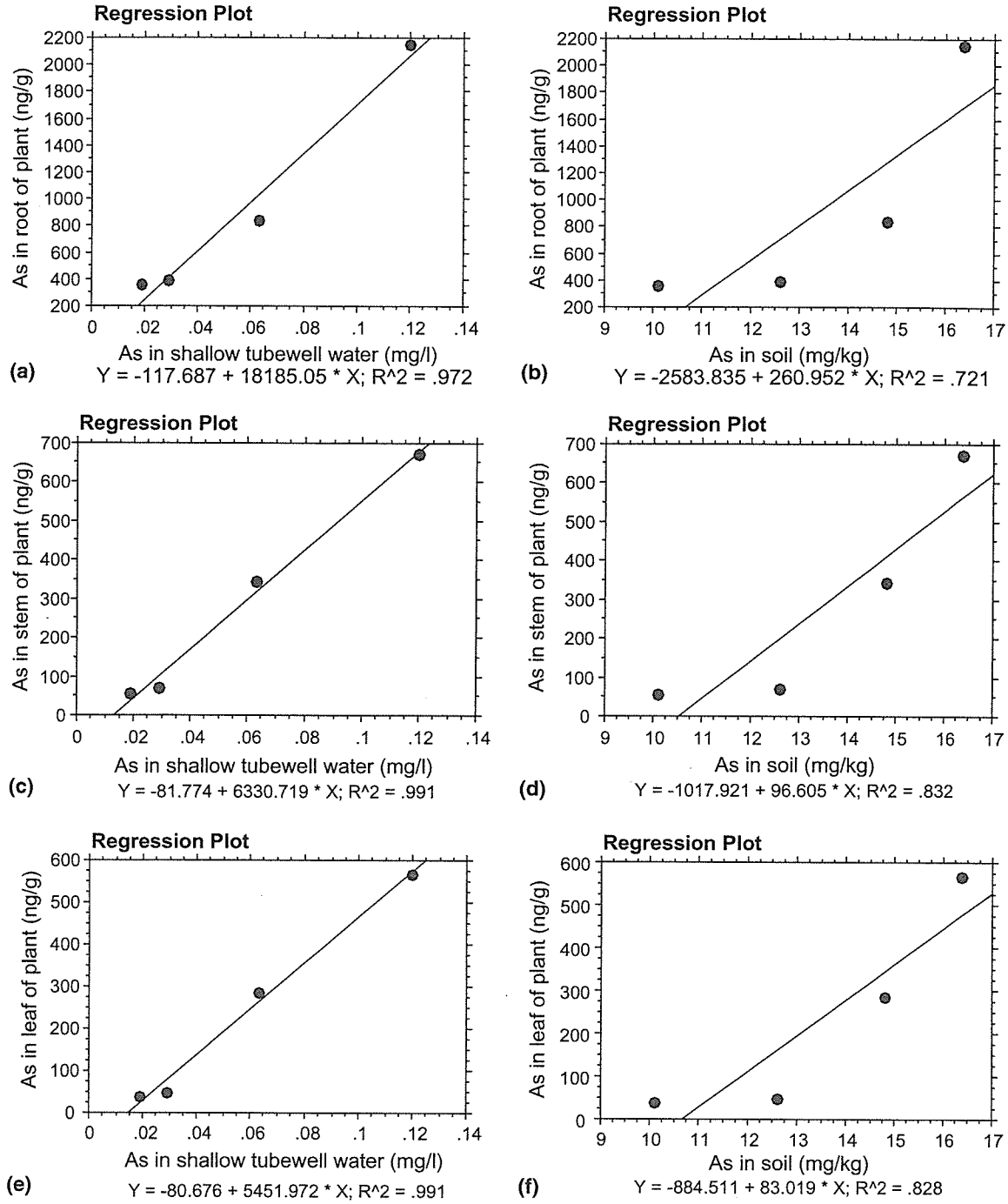


Fig. 4. Regression plots between arsenic in irrigated water and soil vs arsenic in different parts of plants: (a) water vs root, (b) soil vs root, (c) water vs stem, (d) soil vs stem, (e) water vs leaf and (f) soil vs leaf.

root > stem > leaf (Table 3 and Fig. 3). That means arsenic is translocated from root into the aerial organs in amounts decreasing from stem to leaf. It has been reported that the distribution of arsenic in plants, in general, is in descending order from root to stem and leaf to edible parts (Liu et al., 1985). The greatest arsenic accumulation in the blueberry tissue occurred in the roots, from which it was translocated into the aerial organs in amounts decreasing from stems to leaves (Anastasia and Kender, 1973). Approximately 3.1–13.1%, 0.54–4.08% and 0.36–3.45% of arsenic in root, stem and leaf respectively is taken up from the soil in the studied four agricultural lands. Uptake of 7–29% and 17–54% of arsenic in potatoes and carrots respectively grown near a wood preservation factory due to atmospheric deposition around point sources has also been reported (Larsen et al., 1992). The arsenic concentrations in different parts of plants increase with increase of both water

and soil arsenic concentrations (Fig. 3). The positive correlation between the soluble arsenic contents in soil and arsenic contents in root, stem and leaf of the sweet potato plant has been reported (Liu and Gao, 1987). The external contamination of arsenic could not also be ignored. The water, after leaching the surface of plant leaves (most of them are daily diet to the villagers in this area) with an ultrasonic cleaner, contains some amounts of arsenic (mean: 6.93 ng/g, range: <0.04–57 ng/g, $n = 72$). This is due to the fact that the farmers, sometimes used to spray arsenic-contaminated groundwater on the plants, as a result, water on the leaves dries up, leaving a residue of arsenic which with time accumulates on the leaf surface. It has been reported that the water, after leaching the surface of edible herbs with an ultrasonic vibrator, contained significant amounts of arsenic (160 ± 60 ng/g, $n = 10$) (Mandal et al., 1998).

5. Conclusion

State West Bengal is prosperous in agriculture. The state has surplus food production and main crops are paddy, vegetables and cereals. The lands of the nine arsenic-affected districts are very fertile and all are in recent gangetic deltaic plain. Major quantum of food production of West Bengal is coming from these nine districts. The agricultural system is almost groundwater dependent and approximately tens of thousands of small and large-diameter shallow tubewells are in used for agricultural irrigation. The mistakes that the state made in the past that occur even today are the merciless exploitation of groundwater for irrigation without ever trying to adopt effective watershed management to harness its huge surface water resources and rainwater. Till today there is no groundwater withdrawal regulations and agricultural land is flooded with groundwater. Plant actually needs a small fraction of the total water poured to the field. It appears that there is no watershed management system. Now groundwater is considered to be the main source for cultivation and its use is increasing day by day. Even groundwater is the main source for drinking, cooking and other household purposes in these arsenic-affected areas. So, groundwater withdrawal is very high. This heavy withdrawal of groundwater may the reason why iron pyrites decomposes (Das et al., 1996; Roychowdhury et al., 1999; Chakraborti et al., 2001), releases arsenic in water and deposits on soil. So, a part of arsenic, entering in soils from these sources could not be ignored. As a result, soil becomes arsenic-rich. Thus it is expected that arsenic is entering in the food chain from crops cultivated in these areas. In West Bengal and Bangladesh, the surface resources of sweet water such as rivers, wetlands, flooded river basins and oxbow lakes are among the largest in the world. These two delta areas are known as the land of rivers and have approximately 2000 mm annual rainfall. Due to our negligence, most of these water bodies go dry or go water hyacinth. If we can use these water bodies properly for drinking, cooking, agricultural irrigation and other purposes, then we can save the possible arsenic-contamination from groundwater. Moreover, by using pisciculture, duckery, growing vegetables at the bank of these water bodies the economic condition of the villagers will be much better. We could think of using groundwater after a proper use of these available surface water resources. The withdrawal of groundwater must be restricted. Proper watershed management and villager participation are needed to assist in the utilization of these huge bodies of water.

Acknowledgments

We acknowledge the help of 'Japan Society for the Promotion of Science (JSPS)', Ministry of Education, Japan for the financial support to Dr. Tarit Roychowdhury. We further acknowledge 'School of Environmental Studies', Jadavpur University, Kolkata, India for their help during the field survey with us.

References

Aggett, J., Aspell, A.C., 1980. Arsenic contamination in an apple orchard. Environ. Pollut. Ser. A 22, 39–46.

Alam, M.D., Sattar, M.A., 2000. Assessment of arsenic contamination of soils and waters in some areas of Bangladesh. Water Sci. Technol. 42, 185–192.

Alam, M.G.M., Snow, E.T., Tanaka, A., 2003. Arsenic and heavy metal contamination in vegetables grown in Samta village, Bangladesh. Sci. Total Environ. 308, 83–96.

Anastasia, F.B., Kender, W.J., 1973. Influence of soil arsenic on the growth of lowbush blueberry. J. Environ. Qual. 2, 335–337.

Aten, C.F., Bourke, J.B., Martine, J.H., Walton, J.C., 1980. Arsenic and lead in an orchard environment. Bull. Environ. Contam. Toxicol. 24, 108–115.

Chakraborti, D., Basu, G.K., Biswas, B.K., Chowdhury, U.K., Rahman, M.M., Paul, K., Roychowdhury, T., Chanda, C.R., Lodh, D., Ray, S.L., 2001. In: Chappell, W.R., Abernathy, C.O., Calderon, R.A. (Eds.), Arsenic Exposure and Health Effects IV. Elsevier, Amsterdam, pp. 27–52.

Chakraborti, D., Rahman, M.M., Paul, K., Chowdhury, U.K., Sengupta, M.K., Lodh, D., Chanda, C.R., Saha, K.C., Mukherjee, S.C., 2002. Arsenic calamity in the Indian Subcontinent: What lessons have been learned? Talanta 58, 3–22.

Chatterjee, A., Das, D., Chakraborti, D., 1993. A study of groundwater contamination by arsenic in the residential area of Behala, Calcutta, due to industrial pollution. Environ. Pollut. 80, 57–65.

Chowdhury, U.K., 2001. Groundwater Arsenic-contamination Status at Four Geo-morphological Areas in Bangladesh (special reference to arsenic in biological samples and

agricultural crop), Ph.D. Dissertation, Jadavpur University, Kolkata, India, p. 231.

Chowdhury, U.K., Biswas, B.K., Roychowdhury, T., Samanta, G., Mandal, B.K., Basu, G.K., Chanda, C.R., Lodh, D., Saha, K.C., Mukherjee, S.K., Roy, S., Kabir, S., Quamruzzaman, Q., Chakraborti, D., 2000. Groundwater arsenic-contamination in Bangladesh and West Bengal, India. Environ. Health Perspect. 108 (5), 393–397.

Chowdhury, U.K., Rahman, M.M., Mandal, B.K., Paul, K., Lodh, D., Biswas, B.K., Basu, G.K., Chanda, C.R., Saha, K.C., Mukherjee, S.C., Roy, S., Das, R., Kaies, I., Barua, A.K., Palit, S.K., Quamruzzaman, Q., Chakraborti, D., 2001. Groundwater arsenic-contamination and human sufferings in West Bengal, India and Bangladesh. Environ. Sci. 8 (5), 393–415.

Das, D., Samanta, G., Mandal, B.K., Roychowdhury, T., Chanda, C.R., Chowdhury, P.P., Basu, G.K., Chakraborti, D., 1996. Arsenic in groundwater in six districts of West Bengal, India. Environ. Geochem. Health 18 (1), 5–15.

Directorate of Agricultural Engineering, 1991. District data sheet, Minor Irrigation Department, Government of West Bengal, India, p. 21.

Jenkins, D.W., 1980. Vol. 2, Part I, US Environ. Prot. Agency Rep. 600/3–80–090, pp. 30–138.

Kenyon, D.J., Elfving, D.C., Pakkala, I.S., Bache, C.A., Lisk, D.J., 1979. Residues of lead and arsenic in crops cultured on old orchard soils. Bull. Environ. Contam. Toxicol. 22, 221–223.

Larsen, E.H., 1980. Heavy metal pollution of fruit and vegetables grown in the western part of Copenhagen in 1978. Publication 41, The National Food Agency, DK-2860 SØBORG, Denmark.

Larsen, E.H., Moseholm, L., Nielsen, M.M., 1992. Atmospheric deposition of trace elements around point sources and human health risk assessment. II. Uptake of arsenic and chromium by vegetables near a wood preservation factory. Sci. Total Environ. 126 (3), 263–275.

Liu, G.L., Gao, S.R., 1987. The effect of arsenium in red soil on crops. Turang Tongbao 18 (5), 231–233.

Liu, G.L., Cheng, F.X., Gao, S.D., Li, M.Q., 1985. Effect of arsenic in soil on plants. Zhongguo Nongye Kexue (Beijing) 4, 9–16.

Luo, J.F., Xia, Z.L., Li, S.Z., 1991. Chemical behavior of As in purple soils and their effects on crop. Acta Sci. Circumstantiae 11, 269–275.

Mandal, B.K., 1998. Status of Arsenic Problem in Two Blocks Out of Sixty in Eight Groundwater Arsenic-affected Districts of West Bengal, India. Ph.D. Dissertation, Jadavpur University, Kolkata, India, pp. 126, 132.

Mandal, B.K., Roychowdhury, T., Samanta, G., Basu, G.K., Chowdhury, P.P., Chanda, C.R., Lodh, D., Karan, N.K., Dhar, R.K., Tamili, D.K., Saha, K.C., Chakraborti, D., 1996. Arsenic in groundwater in seven districts of West Bengal, India—the biggest arsenic calamity in the world. Curr. Sci. 70, 976–986.

Mandal, B.K., Roychowdhury, T., Samanta, G., Mukherjee, D.P., Chanda, C.R., Saha, K.C., Chakraborti, D., 1998. Impact of safe water for drinking and cooking on five arsenic-affected families for 2 years in West Bengal, India. Sci. Total Environ. 218, 185–201.

Mandal, B.K., Biswas, B.K., Dhar, R.K., Roychowdhury, T., Samanta, G., Basu, G.K., Chanda, C.R., Saha, K.C., Chakraborti, D., Kabir, S., Roy, S., 1999. Groundwater arsenic contamination and sufferings of people in West Bengal, India and Bangladesh: status report up to March, 1998. In: Sarkar, B. (Ed.), Metals and Genetics. Kluwer Academic, Plenum Publishers, New York, pp. 41–65.

Meharg, A.A., Rahman, M.M., 2003. Arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption. Environ. Sci. Technol. 37, 229–234.

National Research Council, 1977. In: Committee on Medical and Biologic Effects of Environmental Pollutants (Ed), Arsenic, National Academy of Sciences, Washington, DC, pp. 16–79.

National Research Council of Canada (NRCC), 1978. Natl. Res. Counc. Can. Publ. NRCC 15391, pp. 1–349.

Queirolo, F., Stegen, S., Restovic, M., Paz, M., Ostapczuk, P., Schwuger, M.J., Munoz, L., 2000. Total arsenic, lead and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. Sci. Total Environ. 255, 75–84.

Roychowdhury, T., 1999. Groundwater Arsenic Contamination of West Bengal, India: Characterization and Chemical Analysis of Bore-hole Sediments, Rotoevaporated Arsenic Rich Water Residue and Status of Three Arsenic-affected Blocks of 24-Parganas (North). Ph.D. Dissertation, Jadavpur University, Kolkata, India, p. 89.

Roychowdhury, T., Basu, G.K., Mandal, B.K., Biswas, B.K., Samanta, G., Chowdhury, U.K., Chanda, C.R., Lodh, D., Roy, S.L., Saha, K.C., Roy, S., Kabir, S., Quamruzzaman, Q., Chakraborti, D., 1999. Arsenic poisoning in the Ganges delta. Nature 401, 545–546.

Roychowdhury, T., Uchino, T., Tokunaga, H., Ando, M., 2002a. Survey of arsenic in food composites from an arsenic-affected area of West Bengal, India. Food Chem. Toxicol. 40, 1611–1621.

Roychowdhury, T., Uchino, T., Tokunaga, H., Ando, M., 2002b. Arsenic and other heavy metals in soils from an arsenic-affected area of West Bengal, India. Chemosphere 49, 605–618.

Schoenhard, G., Koenig, W., 1975. Arsenic contents and effects in soil and plants. Z. Pflanzenkr. Pflazenschutz. 82, 329–336.

Temple, P.J., Linzon, S.N., Chai, B.L., 1977. Contamination of vegetation and soil by arsenic emission from secondary lead smelters. Environ. Pollut. 12, 311–320.

Ullah, S.M., 1998. In: Abstracts: International Conference on Arsenic Pollution of Groundwater in Bangladesh: Causes, Effects and Remedies, 8–12 February, Dhaka Community Hospital, Dhaka, Bangladesh, p. 133.

Walsh, L.M., Sumner, M.E., Keeney, D.R., 1977. Occurrence and distribution of arsenic in soil and plants. Environ. Health Perspect. 19, 67–71.

Wauchope, R.D., McDowell, L.L., 1984. Adsorption of phosphate, arsenate, methanearsenate and cacodylate by lake and stream sediments: comparisons with soils. J. Environ. Qual. 13 (3), 499–504.

Wu, Z.H., Xie, C.G., 1990. Method for analysis of total As, inorganic As and organic As in soil and plant. Nongcun Shengtai Huanjing 2, 57–60.

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Food and Chemical Toxicology 44 (2006) 455–461
www.elsevier.com/locate/foodchemtox

Intake of arsenic from water, food composites and excretion through urine, hair from a studied population in West Bengal, India

T. Uchino [a,*], T. Roychowdhury [a], M. Ando [b], H. Tokunaga [a]

[a] *Division of Environmental Chemistry, National Institute of Health Sciences, 1-18-1 Kamiyoga, Setagaya-ku, Tokyo 158-8501, Japan*
[b] *Musashino University, 1-1-20 Shin-machi, Nishitokyo-shi, Tokyo 202-0023, Japan*

Received 27 May 2005; accepted 19 August 2005

Abstract

To evaluate the main intake source of arsenic by the villagers from arsenic-affected families in Jalangi and Domkol blocks in Mushidabad district, West Bengal—India, we determined the concentrations of arsenic in tubewell water and in food composites, mainly including vegetables and cereals collected from the surveyed families which were cultivated in that region. The daily dietary intakes of arsenic by the villagers were estimated and the excretions of arsenic through urine and hair were determined. The arsenic concentrations in hair and urine of the studied population living in mild (2.78 μg/L), moderate (30.7 μg/L) and high (118 μg/L) arsenic-affected families were 133, 1391 and 4713 μg/kg and 43.1, 244 and 336 μg/L, respectively. The linear regressions show good correlations between arsenic concentrations in water vs hair ($r^2 = 0.928$, $p < 0.001$) and water vs urine ($r^2 = 0.464$, $p < 0.01$). Approximately 29.4%, 58.1% and 62.1% of adult population from mild, moderate and high arsenic-affected families were suffering from arsenical skin manifestations. The mean arsenic concentrations of food composites (vegetables and cereals) in high arsenic-affected families are not significantly different from mild arsenic-affected families. The daily dietary intakes of arsenic from water and food composites of the studied population, living in high, moderate and mild arsenic-affected families were 568, 228 and 137 μg, respectively. The linear regressions show good correlations between arsenic concentrations in hair vs daily dietary intake ($r^2 = 0.452$, $p < 0.001$) and urine vs daily dietary intake ($r^2 = 0.134$, $p < 0.001$). The water for drinking contributed 6.07%, 26.7% and 58.1% of total arsenic in our study from mild, moderate and high arsenic-affected families. The result suggested that the contaminated water from high arsenic-affected families should be the main source for intake of arsenic. On contrary, the contribution of arsenic-contaminated food composites from mild and moderate arsenic-affected families might be the main source for intake of arsenic. The Food and Agriculture Organization/World Health Organization (FAO/WHO) provisional tolerable weekly intake (PTWI) values of arsenic in our study were 3.32, 5.75 and 12.9 μg/kg body weight/day from mild, moderate and high arsenic-affected families, respectively, which is higher than the recommended PTWI value of arsenic (2.1 μg/kg body weight/day).

Keywords: West Bengal—India; Arsenic in tubewell water; Food composites; Human hair and urine; ICP-MS; HPLC

1. Introduction

Groundwater arsenic-contamination and sufferings of people have been reported in West Bengal, India (Chowdhury et al., 2000, 2001; Chatterjee et al., 1995; Das et al., 1994). Out of total 18 districts, 9 districts have been identified where groundwater contains arsenic above 50 μg/L (the Indian permissible limit of arsenic in drinking water). In these 9 arsenic-affected districts, 74 blocks and approximately 2900 villages were arsenic-contaminated. Out of 105,000 water samples from different tubewells in the arsenic-affected areas of West Bengal, about 51% and 25% of the tubewell water samples contained arsenic at above 10 μg/L and 50 μg/L, respectively (Chakraborti et al., 2002). About 89% of the urine samples ($n = 9795$) and 57% of the hair samples ($n = 7135$) contained arsenic above

* Corresponding author. Tel.: +81 3 3700 1141x318; fax: +81 3 3707 6950.
E-mail address: uchino@nihs.go.jp (T. Uchino).

0278-6915/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fct.2005.08.018

its normal level value for urine and toxic levels for hair (Chowdhury et al., 2000). Water, urine and hair samples collected in May 1999. Normal excretion of arsenic in urine ranges from 5 to 40 μg/day (Farmer and Johnson, 1990) and normal level of arsenic in hair ranges from 80 to 250 μg/kg, whereas 1000 μg/kg in the indication of toxicity (Arnold et al., 1990). About 9.7% ($n = 8500$) of the population, screened for arsenic patients ($n = 86{,}000$) have been identified as registered patients with clinical manifestation (Chakraborti et al., 2002). Arsenic-rich pyrites have been identified in the bore-hole sediment samples of Ganges delta in West Bengal (Chakraborti et al., 2001; Roychowdhury et al., 1999). Groundwater is the main source for drinking in these arsenic-contaminated districts. Even the agricultural system is mostly groundwater dependent. For this purpose, all shallow big diameter tubewells were installed for agricultural irrigation. Most of the cases, these shallow tubewells water contained the high concentration of arsenic (Mandal et al., 2001). Million of cubic meters of ground water are used for agricultural irrigation. This heavy withdrawal of groundwater may be the reason why iron pyrites decomposer (Chakraborti et al., 2001; Roychowdhury et al., 1999), releases arsenic in water and deposits on soil. So a part of arsenic could be expected in the food chain, cultivated in these areas. Although drinking water was the main source, but not the only source for intake of arsenic in human body (Mandal et al., 1998). People could consume the arsenic-contaminated water during washing of food composites, washing their mouth after eating and cleaning utensils. Murshidabad is one of the nine arsenic-affected districts in West Bengal (Chowdhury et al., 2000). Both Jalangi and Domkal blocks are severely arsenic-contaminated areas where people with arsenic skin lesions have been reported (Mandal et al., 1996). The area and population of Jalangi and Domkal blocks are 122 sq. km, 304.2 sq. km and 173,056, 253,349, respectively (according to 1991 census). The food composites were divided into two categories. These are vegetables and cereals. Most of the vegetables and other food composites were cultivated in this area and entered to the local market. Those who have individual agricultural lands used to collect the food composites from their own lands.

In this study, we investigated the total arsenic present in the tubewell water, and food composites collected from 37 families that lived in two arsenic-contaminated blocks, Jalangi and Domkal of Murshidabad district. The aim of this study is to determine the intake of total arsenic coming from water and food composites and excretion through urine and hair for the studied family members.

2. Materials and methods

2.1. Instrumentation

A microwave digestion system (CEM Corporation, MARS 5) was used for sample digestion of food composites and hair. An inductively coupled plasma mass spectrophotometer (ICP-MS) (Hewlett–Packard 4500) was used as a chromatographic detector. The ICP-MS system was equipped with a Shimadzu LC-10ADVP liquid chromatographic solvent delivery pump and a double-pass, Scott-type spray chamber (water cooled, 20 °C) (ORION, RKS-1500V-C). The instrumental conditions were as follows: RF power; 1240 W, RF refraction current; 5 W, RF matching; 1.23 V, sample depth; 6 mm, sample Sukimmer Corn; Ni, monitoring mass; m/z 75(As) and 77($ArCl^+$), integrating interval; sec. scan number; one time, argon flow rate; plasma 15 L/min, auxiliary 0.8 L/min, Nebujxlizer 0.8 L/min.

Detection limit of arsenic in our system is 0.04 μg/L. Off-line data from the ICP-MS were processed with special chromatographic software. HPLC-ICP-MS (Hewlett–Packard 7500) system was used as a chromatographic detector of urine and the analytical method for arsenic metabolites in urine was described the papers of Tokunaga et al. Tokunaga et al. (2002, 2003, 2005).

2.2. Chemicals and reagents

All reagents were of analytical grade. MilliQ water (Yamato Millipore-filter, WT 100) was used throughout. Stock solution of arsenic trioxide (As_2O_3) with concentration of 1000 mg/L (Cica-Reagent, Chuo-Ku, Tokyo, Japan) was used for the standard solutions preparation for ICP-MS. Initially a standard solution of 10 mg/L was prepared from the stock solution (1000 mg/L) using a mixture solution of nitric acid (12%) and hydrogen peroxide (8%). The same ratio of adding nitric acid and hydrogen peroxide were maintained during the sample preparation. Then, a standard solution of 1 mg/L was prepared, directly from the 10 mg/L standard, using the same mixture solution. Finally, the aliquots of 0.1 μg/L, 0.5 μg/L, 1 μg/L, 5 μg/L, 10 μg/L, 20 μg/L, 50 μg/L, 100 μg/L, 200 μg/L and 500 μg/L were prepared, stock solutions were kept in polyethylene bottles and kept at 4 °C. The standard solutions were prepared daily for analysis. The calibration curves were established with the standard solutions.

The sample digestions were carried out with concentrated nitric acid (Wako Pure Chemical Industries Ltd., Osaka, Japan, No. 140-04016) and high purity hydrogen peroxide (35.5%) (Wako Pure Chemical Industries Ltd., Osaka, Japan, No. 085-04056). Rice flour (SRM 1568a) and wheat flour (SRM 1567a) from the National Bureau of Standards (NBS), Gaithersburg, MD 20899, USA, apple leaves (SRM 1515) and tomato leaves (SRM 1573a) from the National Institute of Standards and Technology (NIST), (Gaithersburg, MD 20899, USA) were used as Standard Reference Materials. The standard hair (NCS DC 73347) was purchased from China National Analysis Center for Iron and Steel (Beijing, China). To check whether our analytical results agree with standard reference materials, the SRM samples were analyzed after digesting and under the same manners as the samples. The observed values of arsenic were as follows: rice flour (SRM 1568a); 0.28 ± 0.05 μg/g (certified value 0.29 ± 0.03 μg/g); wheat flour (SRM 1567a); 0.006 ± 0.001 μg/g (certified value 0.006 ± 0.001 μg/g); apple leaves (SRM 1515); 0.032 ± 0.004 μg/g (certified value 0.38 ± 0.007 μg/g); tomato leaves (SRM 1573a); 0.098 ± 0.007 μg/g (certified value 0.112 ± 0.004 μg/g); human hair (NCS DC 73347); 0.28 ± 0.03 μg/g (certified value 0.28 ± 0.04 μg/g). The observed values were in good agreement with the certified values.

2.3. Sample collection and preparation

Water, food composites, urine and hair were collected from 12 arsenic-affected Families (a, b, c, d, e, f, g, h, i, j, k and l; shown in supplementary Table 1-1) in Chak Chaitanya, Ramnarayanpara and Fakirabad villages of Jalangi block during December 2000 and 25 arsenic-affected families (A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P,Q, R, S, T, U, V, W, X and Y; shown in supplementary Table 1-2) in Shrikrishnapur, Mamudpur and Bakshipur villages of Domkol block in Murshidabad district, during February 2001. Most of the food composites were cultivated in this area and bought in the local market. The collected samples are shown in Table 1. Water samples were collected from the hand tubewells, used for mainly drinking by the families. The water samples were not filtered during

Table 1
Sample collection from Jalangi and Domkal block

	Jalangi block	Domkal block
Date	December 4–7, 2000	February 20–22, 2001
Village	Chak Chaitanya, Ramnarayapara and Fakirabad	Shrikrishnapur, Mamudpur and Bakshipur
Samples	Tubewell waters: 7 Vegetables (potato, onion, garlic, arum leaf, spinach, leaf of vegetables, radish, green banana and papaya): 37 Cereals (rice, wheat flour, lentil, pulse): 29 Hairs: 51	Tubewell waters: 9 Vegetables (potato, onion, garlic, green chili, arum leaf, lemon, leaf of vegetables, green banana, bittergourd and green turmeric): 69 Cereals (rice, wheat flour, lentil, peas dal, pulse item, biscuit): 46 Hairs: 96

collection or prior to analysis, stored in polyethylene bottles, and nitric acid (0.1% v/v) was added as preservative.

After collection, the food composites were placed in plastic bags individually. The water samples and food composites were kept in a cold icebox and transported to our laboratory by air. They were kept in refrigerator at −30 °C and 4 °C, respectively, until further treatment. After keeping at room temperature for several hours, most of the vegetables were cut by pieces. The skin of the potato was removed and finally cut by pieces. The surface layers of the onion and garlic were peeled off and the inside layer was taken for further treatment. All the vegetables (contain approximately 80% moisture) and cereals like raw rice, wheat and pulses were washed with de-ionized water in an ultrasonic cleaner (50/60 Hz, Model No. B-220, BRANSON, USA). All the food composites were dried in open air under diffused sunlight for 24 h, followed by drying in an oven at 50 °C for complete dryness, manually ground to a fine powder (homogenized) with a mortar and pestle and then passed through a 30-mesh sieve.

Spot urine samples were collected from the surveyed family members and kept in polyethylene centrifuge tubes. After collection, the samples were stored in a cold icebox and transported to our laboratory by air. Finally the samples were kept in a refrigerator at −30 °C before use.

Hair sample was collected from the studied family members. The sample was collected from the top using a scissor (we did not get scalp hair) and kept it individual plastic container. Brought to our laboratory, washed with MilliQ water, followed by acetone using ultrasonic sonicator for 10 min each and finally were dried in an oven at 50 °C.

2.4. Digestion procedures

Approximately 0.5 g of dry, finely powdered food sample or about 10–30 mg of hair sample was weighed into a dry, clean Teflon digestion vessel. Two millilitre of milliQ water, 3 mL of concentrated nitric acid and 2 mL of hydrogen peroxide were added. Hair sample was allowed for one night stay at room temperature. The vessel was closed, placed into the rotor and tightened. The loaded rotor having maximum 7 vessels per single time was placed into the microwave oven. The microwave conditions for digestion of food composites and hair are summarized in Table 2. After cooling for 30 min, the vessels were opened carefully. Each digested solution was transferred to a 25-mL volumetric flask and made up with milliQ water. Finally it was filtered through a milli-pore membrane (0.45 μm) and kept in plastic container for analysis.

Table 2
Microwave-oven condition of digestion for food composites and hairs

Stage	1	2	3
Oven condition for food composites			
Power (%) (600 W)	100	100	100
PSI	100	130	160
RAMP (min)	20	10	10
HOLD (min)	10	10	10
Oven condition for hairs			
Power (%) (600 W)	100	100	100
PSI	80	120	150
RAMP (min)	20	5	5
HOLD (min)	10	10	10

3. Estimation of total intake of arsenic

Rice and vegetables are the main food composites for the villagers. Normally, the villagers eat rice with vegetables three times per day. They cook vegetables with spices at hot taste. Green chili and onion is very common with every meal.

Sometimes they take pulses with rice and vegetables. Rarely they eat bread (made from wheat flour). Villagers occasionally eat fish (once per week), egg (once per week) and meat (once per month). The average water intakes per day for adult males, adult females and children (around 10 years of age) are 4 L, 3 L and 2 L, respectively. Normally daily typical average food intakes for the villagers at each meal (Chowdhury et al., 2001) were as follows:

Meal	Group	Type of food	Average quantity of consumption
Breakfast	Adult (male and female)	Pantavat* with vegetables	Rice: 250 g, vegetables: 100 g
	Children	Pantavat with vegetables	Rice: 100 g, vegetables: 100 g
Lunch	Adult (male and female)	Rice and vegetables	Rice: 250 g, vegetables: 200 g
	Children	Rice and vegetables	Rice: 150 g, vegetables: 100 g
Dinner	Adult (male and female)	Rice and vegetables	Rice: 250 g, vegetables: 200 g
	Children	Rice and vegetables	Rice: 150 g, vegetables: 100 g

* Pantavat: The villagers take it as their daily breakfast. They pour water on cooked rice (2:1 ratio) and keep it for overnight. Next day morning, they eat it mainly with green chili, onion and salt, sometimes with vegetables and fried potatoes.

Total intake of arsenic by adult male (μg) = 4 × (As conc. in tubewell waters) + 0.75 × (As conc. in cereals) + 0.5 × (As conc. in vegetables).
Total intake of arsenic by adult female (μg) = 3 × (As conc. in tubewell waters) + 0.75 × (As conc. in cereals) + 0.5 × (As conc. in vegetables).
Total intake of arsenic by children (μg) = 2 × (As conc. in tubewell waters) + 0.45 × (As conc. in cereals) + 0.3 × (As conc. in vegetables).

4. Results and discussion

In this study, our surveyed population consisted of 26 males and 25 females from 12 families (a–l) in Chak chaitanya, Ramnarayapara and Fakirabad villages of Jalangi block, 44 males and 40 females from 21 families (A–U) in Shrikrishnapur, and Mamudpur villages of Domkal block and 5 males and 7 females from 4 families (V–Y) in Bakshipur village of Domkal block. The arsenic symptom, sex, age of each person, the arsenic concentrations in tubewell water, hair and urine of the studied population from Jalangi and Domkal blocks were shown in supplementary Tables 1-1 and 1-2, respectively. As symptoms was indicated by dermatologist with us. The parametric presentation of arsenic concentrations in hair and of the studied population living in mild (less than 10 μg/L), moderate (between 10 and 50 μg/L) and high (above 50 μg/L) arsenic-affected families were shown in Table 3.

Regression analyses have been carried out between the arsenic concentrations in water and arsenic concentrations in hair/urine of the studied population. The linear regressions showed arsenic concentrations in water vs hair ($r^2 = 0.928$, $p < 0.001$) (Fig. 1) was higher than water vs urine ($r^2 = 0.464$, $p < 0.01$) (Fig. 2). Approximately 29.4%, 58.1% and 62.1% of adult population from mild, moderate and high arsenic-affected families were suffering from arsenical skin manifestations. The arsenic concentrations in food composites in Jalangi and Domkol blocks were shown in supplementary Table 2. The mean arsenic concentrations of food composites (vegetables and cereals) in high and moderate arsenic-contaminated waters were not significantly different from mild arsenic-contaminated waters. The mean arsenic concentrations of vegetables obtained from the families using the high, moderate and mild arsenic-contaminated waters, were 80, 74 and 67 μg/kg, respectively. The mean arsenic concentrations of cereals obtained from the families using the high, moderate and mild arsenic-contaminated waters, 253, 239 and 150 μg/kg, respectively. D'Amato et al. reported that inorganic arsenic contributed about 70% total arsenic in samples of Arborio rice (D'Amato et al., 2004). Vela et al. reported that inorganic arsenic and dimethylarsinic acid (DMA)-were the main species found in rice-based and mixed rice/formula cereals, although traces of methylarsonic acid (MMA) and that only inorganic arsenic was present in freeze-dried sweet potatoes, carrots, green beans and pea-

Table 3
Parametric presentation of arsenic concentration in tube-wells water and hair from arsenic-contaminated area in Jalangi and Domkal block

	As in tubewell waters (μg/L)				As in hair (μg/kg)				Symptom ratio of adults	Age of villagers	
	n	Mean ± SD	Median	Range	*n*	Mean ± SD	Median	Range		*n*	Mean ± SD
Mild arsenic-contaminated water (As in water 0–10 μg/L)	5	2.78 ± 2.72	2.58	0.64–7.30	28	133 ± 301	0	0–1345	5/17 (29.4%)	28	24 ± 16
Moderate arsenic-contaminated water (As in water 10–50 μg/L)	6	30.7 ± 12.3***	30.6	16.0–48.1	78	1391 ± 1221***	958	122–5607	25/43 (58.1%)	78	21 ± 15
High arsenic-contaminated water (As in water 50 μg/L)	5	118 ± 51**,##	115	72.6–170	41	4713 ± 3929***,###	3316	1139–15,864	18/29 (62.1%)	41	23 ± 15

Significantly different from mild arsenic-contaminated water, $^{**}P < 0.01$, $^{***}P < 0.001$.
Significantly different from moderate arsenic-contaminated water, $^{\#\#}P < 0.01$, $^{\#\#\#}P < 0.001$.