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Total arsenic, arsenic species, and trace elements in crop and vegetable grown in areas irrigated with arsenic contaminated water in Bangladesh and West Bengal-India

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ABSTRACT

In this study, tube well water, soil, crop, and vegetable were collected from agricultural field where irrigated with arsenic contaminated water. Estimation of total arsenic and other metals and metalloids in soil, vegetable, and paddy (rice & husk) samples by using ICP-MS after microwave digestion. But arsenic species in paddy (rice + husk), rice, husk, and vegetable by IC-ICP-MS after TFA extraction.

Results show that the average arsenic concentration in contaminated soil, rice, and vegetable were 3.81, 3.62, and 5.66 times higher than the control samples, respectively. The overall observations indicated that arsenic concentration in vegetable and paddy were positively correlated with arsenic in soil. Also, for paddy arsenic concentration decreases shoot > seed (rice) > husk and in vegetables the distribution is leaf> stem > fruit.

The regression analysis was carried out between arsenic and other metals in soil samples. However, no significant co-relation was observed between As & Mn, As & Cu, As & Ni, or As & Pb. But a significant (<0.05) positive correlation found between As & Zn (r =+0.763, p = 0.027) and also a strong negative correlation was observed between As & Hg (r = -0.802, p = 0.009).

Arsenic along with Se, Mn, Cu, Hg, Pb & Ni were analyzed in rice & husk of 3 paddy samples cultivated with arsenic contaminated water. The regression analysis was carried out between arsenic and other metals. Linear regression shown negative correlation between As & Se (r= -0.999, p = 0.018), As & Pb (r = -0.992, p = 0.078) and positive correlation between As & Cu (r =+0.998, p = 0.03). But no satisfactory correction observed between As & Mn, As & Hg, and As & Ni. It has been observed selenium concentration decreases with increase arsenic concentration in both rice and husk, collected from As contaminated field in Bangladesh. This has also been observed in two vegetable samples those we had studied. All analyzed elements concentration (µg/gm) were less in “Kachu (Taro)” comparing “Data (Stem amaranth)” except arsenic. Arsenic was very high in “Kachu” comparing “Data” even though they were irrigated with same water containing arsenic 205 µg/L.

The overall conclusion from arsenic species analysis in rice, paddy (rice + husk), and some vegetables are that inorganic arsenic is the dominating species of arsenic. It appears from all four-rice analysis that inorganic arsenic is the major portion of arsenic in rice. All four-husk analysis shows only presence of inorganic arsenic. No methylated form of arsenic was found in any husk samples, but arsenic species in a paddy (rice+ husk) sample shows high inorganic arsenic (76.46%) and 19.37% DMA & 4.23% MMA. It shows presence of inorganic arsenic & DMA, and possibility of an unknown arsenic species in Lady's Finger. It was very high arsenic concentration in a vegetable named "Kachu" which grows inside soil a popular food in West Bengal-India and Bangladesh. Most interesting, its inorganic arsenic concentration is quite high, but it has no detectable amount of methylated form of arsenic and possible of an unknown arsenic species.

Rice and vegetable are the staple food for poor villagers of Bangladesh and West Bengal-India. This is true for the villagers in Kolsur gram-panchayet (G.P.) in Deganga block of North 24-Parganas district, West Bengal-India, where we studied for arsenic in soil, rice, and vegetable from 10 plots cultivated with arsenic contaminated water. From the results of total arsenic [(drinking water + rice + vegetable + Pantavat (rice mixed with water) + water added for food preparation)] body burden to North Kolsur villagers is 1185.0 µg for per adult per day and 653.2 µg for per child per day. Amount of arsenic coming from rice, vegetable, and water added for Pantavat and food preparation is 485 µg i.e., 41% of total for adult and 253.2 µg i.e., 38.8% for child, and from rice and vegetable 285 µg i.e., 24% of total for adult and 153.2 µg i.e., 23.4% for child (around age 10 years). Our findings show most of the arsenic coming from food is inorganic in nature. As toxicity of most of the organic arsenic compounds in food is less compared to inorganic arsenic.

Therefore, compared to worldwide arsenic consumption from food, it appears Kolsur villagers are also consuming high amount of inorganic arsenic from food and vegetable, and people appears also at risk from arsenic in food. Kolsur village is an example of many such villages in West Bengal-India and Bangladesh.

Further, products from arsenic irrigated water- soil system rich in arsenic are also coming to common marketplace far away from contaminated areas and even people who are not drinking arsenic contaminated water may get arsenic from food products produced from contaminated fields. In West Bengal-India and Bangladesh rice, vegetable, and other products are coming to cities (including Kolkata in West Bengal-India and Dhaka in Bangladesh) from villages and possibility that city people consuming arsenic contaminated products from contaminated areas cannot be ruled out.

Abbreviation: IC-ICP-MS,Ionchromatography-inductivelycoupledplasma-Massspectrophotometry; FI-HG-AAS, Flow injection-hydride generation -atomic absorption spectrometry

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Introduction

In West Bengal-India out of its total 18 districts in 9 districts arsenic in groundwater has been found over 50 µg/L. Total area and population of these 9 districts are 38,865 km2 and 42.7 million (approx.), respectively while the area and population of West Bengal are 88,000 km2 and 68 million (approx.). This does not mean that 42.7 million people in these 9 districts are drinking arsenic contaminated water and will suffer from arsenic toxicity, but no doubt they are at risk. In 9 affected districts of West Bengal, approximately 6 million people are drinking arsenic contaminated water at levels >50 µg/L. For arsenical skin lesions, we examined approx. 86,000 people in 7 affected districts out of 9 and 8500 (9.8%) people were registered with arsenical skin lesions. But we expect, from extrapolation of our generated data that nearly 300,000 people may have arsenical skin lesions in West Bengal-India.

State, West Bengal is prosperous in agriculture. The state has surplus food production and main crops are paddy and vegetable. Land of these 9 contaminated districts of West Bengal is very fertile and all are in recent gangetic deltaic plain. Major quantum of food production of West Bengal-India is coming from these 9 districts and tens of thousands of small and big diameter tube wells are in use for irrigation purpose. Plant needs a small fraction of the total water we pour to the field. Groundwater is considered to be the main source of water for agriculture and its use is increasing day by day. It has been noticed that even if surface water is available for irrigation from nearing source farmers are reluctant to use those sources if they must spend some extra money for this purpose. Except 5 months of rainy season (June-October) rest of the 7 months of the year farmers use groundwater for agriculture. Even during June to October if there are no rain farmers use groundwater.

During 1996 it has been reported[1] by School of Environmental Studies (SOES), Jadavpur University, Kolkata that from a single Rural Water Supply Scheme (RWSS), Govt. of W. Bengal in Malda district, supplying water to a few villages, and 147.8 kg of arsenic came out during a year with groundwater. Therefore, it is expected that huge quantity of arsenic is falling on agricultural land from contaminated tube wells in use for irrigation. A follow-up study was made by SOES to know how much arsenic is falling on irrigated land in one year during cultivation from all 3200 tube wells that exist in the block Deganga of North 24-Parganas[2]. The basis of calculation was like this: 3200 shallow tube wells of 7 cm to 10 cm diameter were used in 1997 in Deganga block for agriculture and average discharge rate was 20 m^3/hr. electric / diesel pumps (average 5HP) were used. These shallow tube wells used to run in average 7 hours per day for 7 months in a year. We had analyzed 597 irrigation tube wells out of total 3200. Out of those 597 tube wells, 574 tube wells contain arsenic ≥10 µg/L. The average arsenic concentration of the 574 tube wells was 70 µg/L (range 10 -840 µg/L). A calculation was made to know how much arsenic is falling on soil from 3200 tube wells based on measurement of 574 tube wells (total analyzed) and extrapolating to 3200. The overall result shows from the block Deganga alone 6.4 tons of arsenic is falling on agricultural land in one year from 3200 agriculture tube wells. Thus, it appears that in West Bengal-India and Bangladesh a few thousand tons of arsenic is falling on agricultural land in every year.

Total arsenic contribution through food for many developed countries have been reported[3]. Although sea food contains mainly nontoxic organic forms of arsenic and rapidly excreted through urine, but other than sea food inorganic arsenic may be the major contribution of arsenic in many foods. A study from Canada[4,5] indicates that arsenic content of many foods is mainly inorganic in nature and typically in the range 65-75%. US-EPA reported that percentage of inorganic arsenic in rice, vegetables and fruits are 35%, 5%, and 10%, respectively[6]. It is reported that absorption of arsenic by plant is influenced by the concentration of arsenic in soil[7].

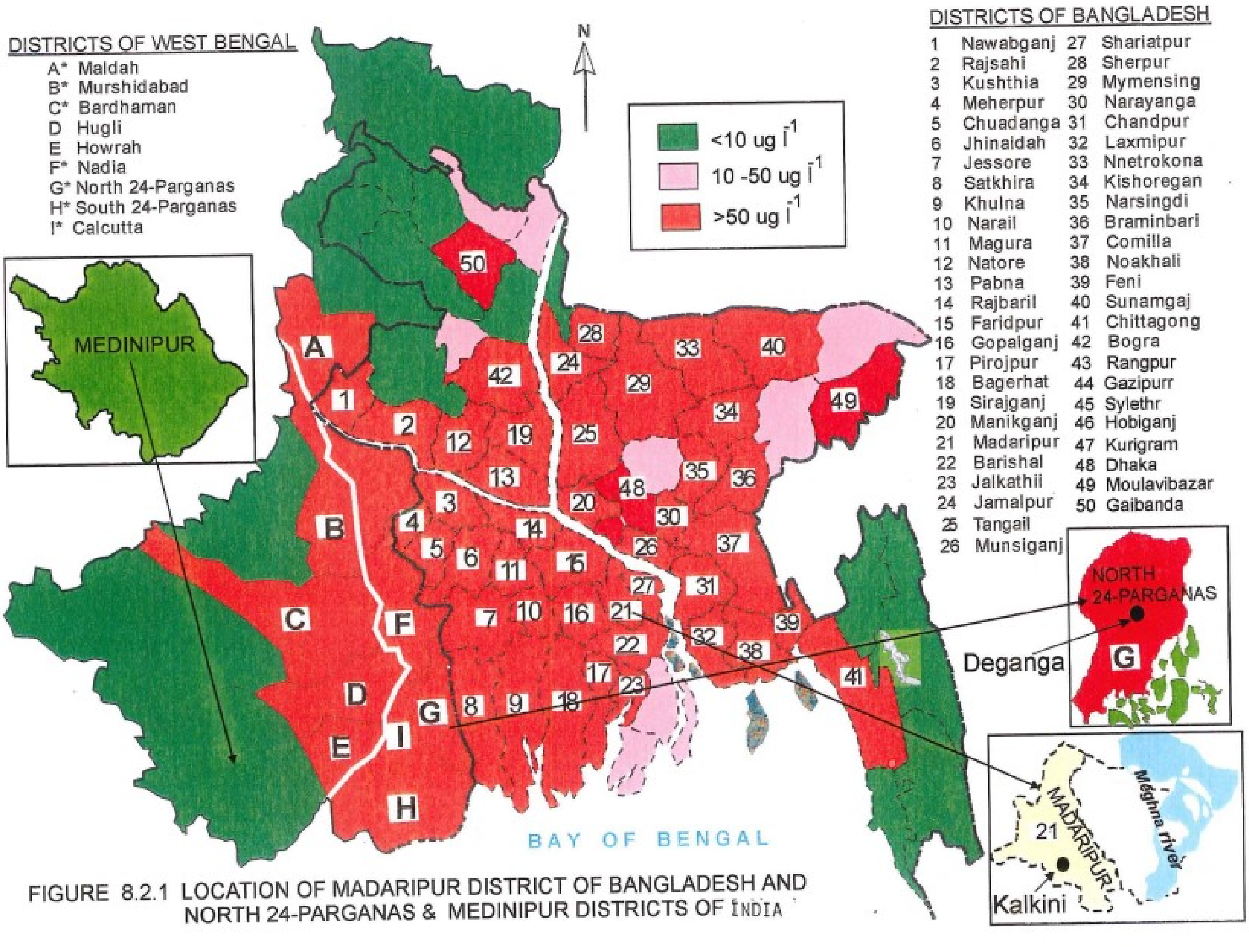


Figure 1. Location of Madaripur district of Bangladesh, and North 24-Parganas and Medinipur districts of India

In arsenic affected areas of West Bengal-India and Bangladesh huge quantity of arsenic is falling on agricultural land and thus it will be interesting and very important to know whether there is an increase concentration of arsenic in vegetable and crops that grow in this region.

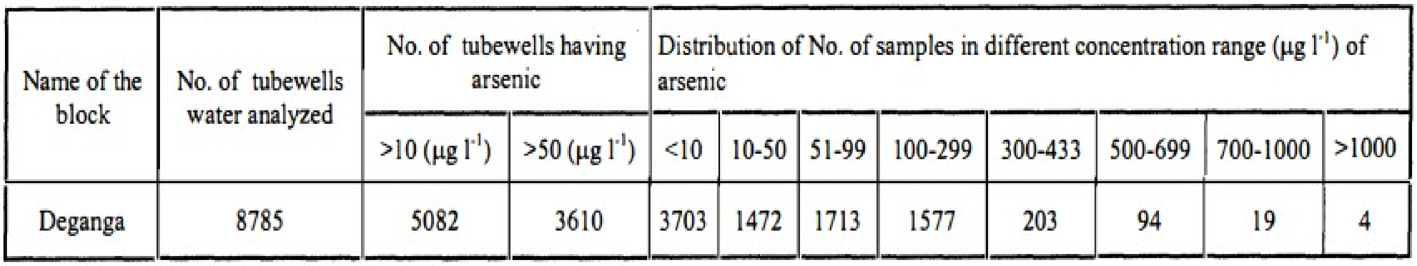
In this paper, I will report (a) the total arsenic concentration in soil, paddy (shoot, rice and husk), vegetable (including edible root, stem, leaf, and fruit) in 10 plots of land irrigated with arsenic contaminated water, (b) arsenic species in paddy (rice + husk), rice, husk, and in vegetable (also in edible root, stem, and fruit), (c) some metals and metalloids in soil, vegetable, rice.and husk, and (d) Arsenic body burden.

METHODS AND MATERIALS

Selection of study area

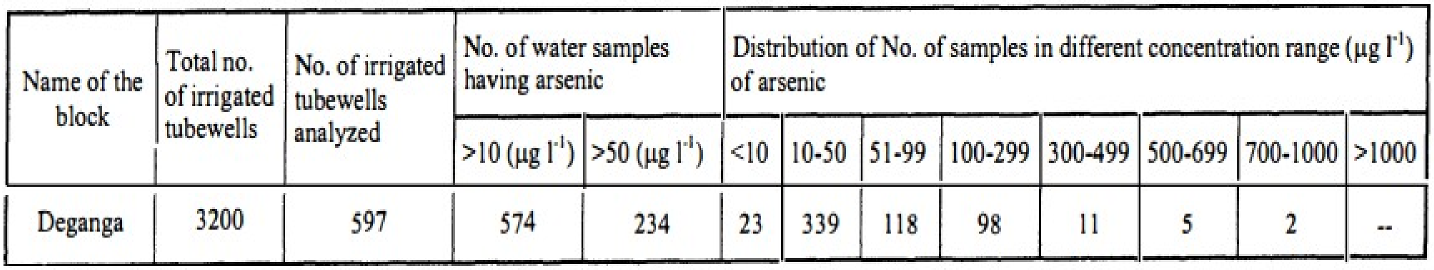
Demography of the State West Bengal is 18 administrative districts and North 24- Parganas is one of the districts. North 24-Parganas is one of the 9 arsenic affected districts of West Bengal-India also. In North 24-Parganas there are 22 blocks/ police stations. Each block has several Gram Panchayets (G.P.) and in each G.P., there are several villages. We have chosen Deganga block of North 24- Parganas district as our study area. The reasons are, (A) we have the detail 8785 hand tube-wells water analysis report of Deganga one of the 22 blocks of North 24-Parganas (Table 1) and also 597 irrigation tube wells report out of 3200 which were used for irrigation in Deganga block alone (Table 2), (B) Deganga block is close (about 60 km) from our institute (SOES) with good road connection, and (C) we are working in this block for a long time and have good report with the villagers. Figure 1 shows arsenic affected block of North 24-Parganas and Deganga block. Deganga block has 13-gram panchayets and groundwater of all these gram pahchayets are arsenic contaminated (>50 µg/L). Out of 13-gram panchayets (G. P.), in 11 G. Ps we have identified patients with arsenical skin lesions. We had chosen 10 fields in Kolsur (North) village of Deganga block under Kolsur gram panchayet. Table 3 shows the crops from 10 fields we had analyzed and other related information. For control study, we had chosen the district Medinipur, an area was groundwater arsenic concentration <3 µg/L; soils of the control area show arsenic in the range 5.31 µg/gm to 6.60 µg/gm (n=6). Overall information of control area is given in Table 4.

Table 1: Distribution of arsenic in tube wells water in Deganga, North 24-Parganas, West Bengal, India



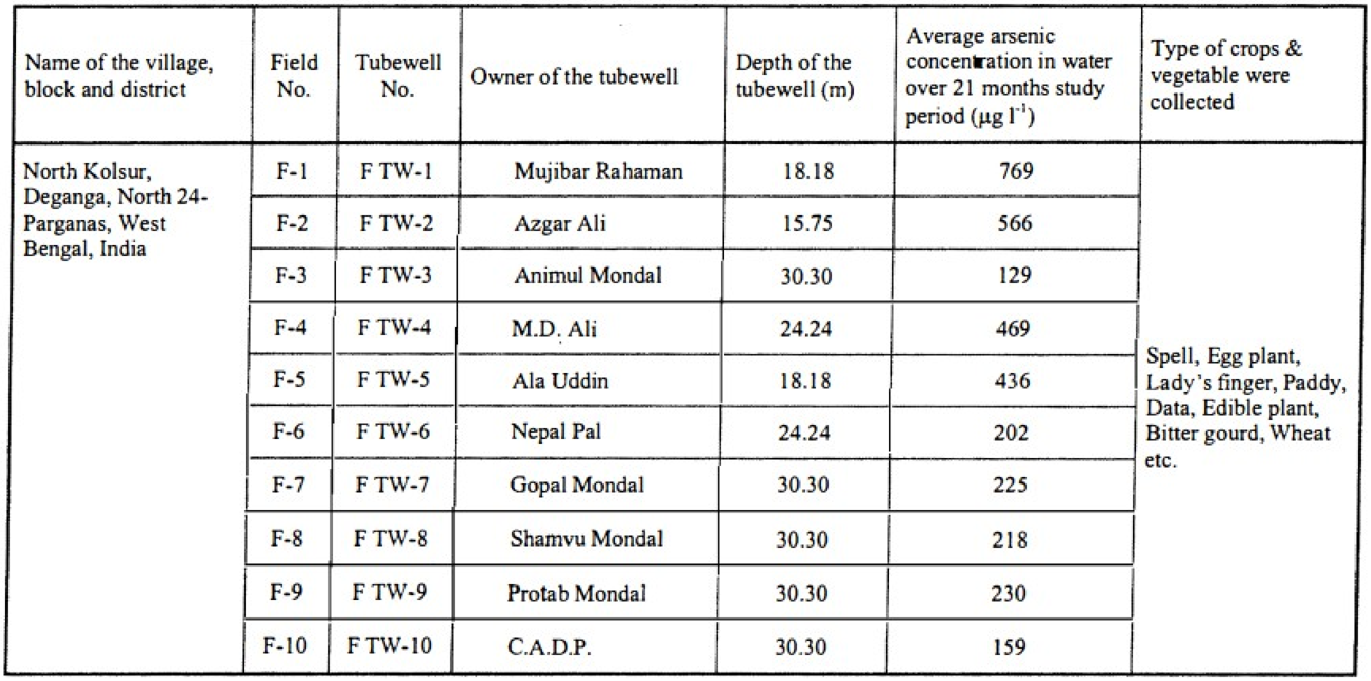
Name of the block	No. of tubewells water analyzed	No. of tubewells having arsenic		Distribution of No. of samples in different concentration range ($\mu g\ l^{-1}$) of arsenic							
		>10 ($\mu g\ l^{-1}$)	>50 ($\mu g\ l^{-1}$)	<10	10-50	51-99	100-299	300-433	500-699	700-1000	>1000
Deganga	8785	5082	3610	3703	1472	1713	1577	203	94	19	4

Table 2: Distribution of arsenic in irrigated tube wells water in Deganga block, North 24-Parganas, West Bengal-India



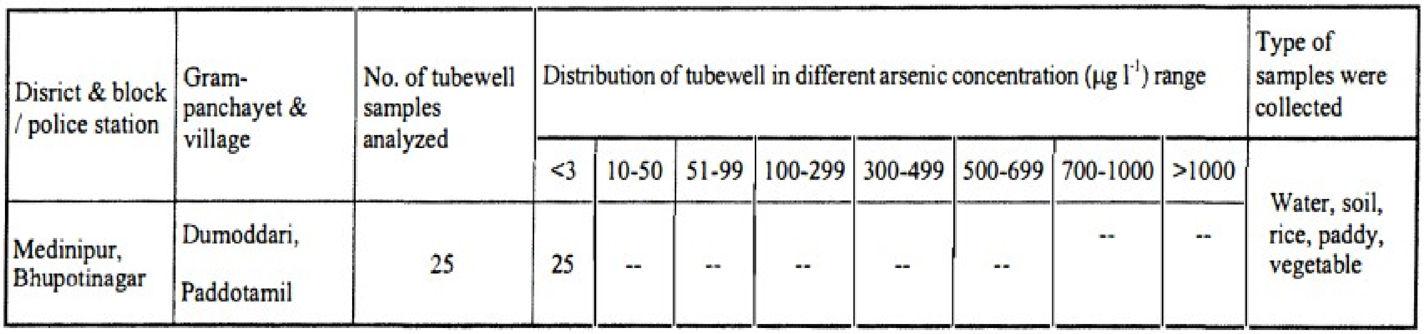
Name of the block	Total no. of irrigated tubewells	No. of irrigated tubewells analyzed	No. of water samples having arsenic		Distribution of No. of samples in different concentration range ($\mu g\ l^{-1}$) of arsenic							
			>10 ($\mu g\ l^{-1}$)	>50 ($\mu g\ l^{-1}$)	<10	10-50	51-99	100-299	300-499	500-699	700-1000	>1000
Deganga	3200	597	574	234	23	339	118	98	11	5	2	--

Table 3: Type of crops and other information of 10 selected agricultural fields in Kolsur village of Deganga block, West Bengal, India where arsenic contaminated ground water was used for irrigation purpose.



Name of the village, block and district	Field No.	Tubewell No.	Owner of the tubewell	Depth of the tubewell (m)	Average arsenic concentration in water over 21 months study period ($\mu g\ l^{-1}$)	Type of crops & vegetable were collected
North Kolsur, Deganga, North 24-Parganas, West Bengal, India	F-1	F TW-1	Mujibar Rahaman	18.18	769	Spell, Egg plant, Lady's finger, Paddy, Data, Edible plant, Bitter gourd, Wheat etc.
	F-2	F TW-2	Azgar Ali	15.75	566	
	F-3	F TW-3	Animul Mondal	30.30	129	
	F-4	F TW-4	M.D. Ali	24.24	469	
	F-5	F TW-5	Ala Uddin	18.18	436	
	F-6	F TW-6	Nepal Pal	24.24	202	
	F-7	F TW-7	Gopal Mondal	30.30	225	
	F-8	F TW-8	Shamvu Mondal	30.30	218	
	F-9	F TW-9	Protab Mondal	30.30	230	
	F-10	F TW-10	C.A.D.P.	30.30	159	

Table 4: Overall information of control area, where groundwater contains arsenic below 3 µg/L

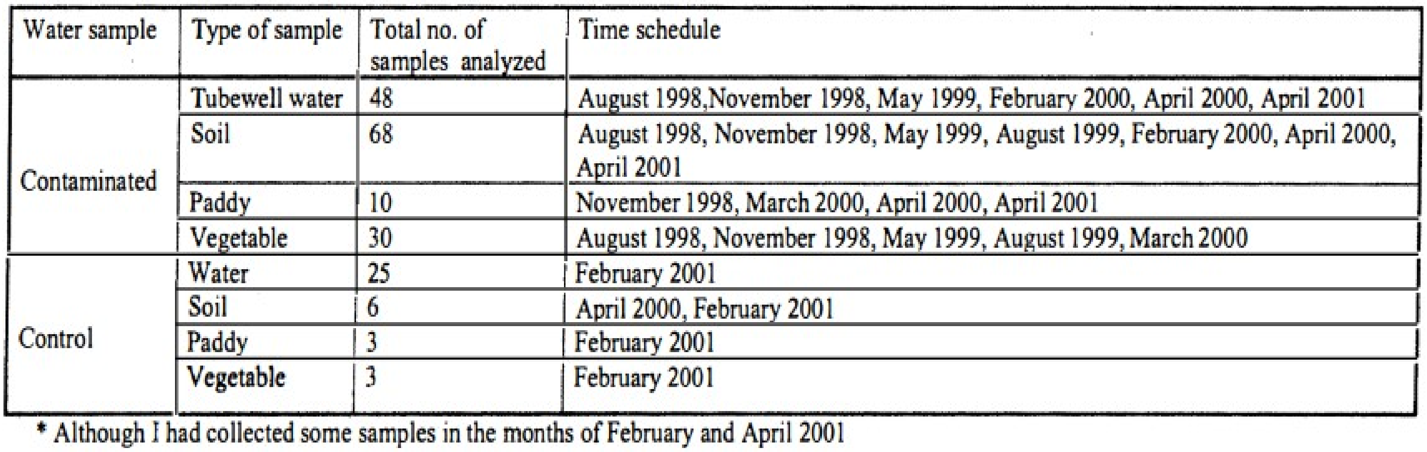


Disrict & block / police station	Gram-panchayet & village	No. of tubewell samples analyzed	Distribution of tubewell in different arsenic concentration ($\mu g\ l^{-1}$) range								Type of samples were collected
			<3	10-50	51-99	100-299	300-499	500-699	700-1000	>1000	
Medinipur, Bhupotinagar	Dumoddari, Paddotamil	25	25	--	--	--	--	--	--	--	Water, soil, rice, paddy, vegetable

21 months study report

Studies had been carried for 21 months (August 1998 to April 2000). Table 5 shows the number of samples and time schedule of the whole study.

Table 5: The number of samples and time schedule of the whole study (from August 1998 to April 2000) *



Water sample	Type of sample	Total no. of samples analyzed	Time schedule
Contaminated	Tubewell water	48	August 1998,November 1998, May 1999, February 2000, April 2000, April 2001
	Soil	68	August 1998, November 1998, May 1999, August 1999, February 2000, April 2000, April 2001
	Paddy	10	November 1998, March 2000, April 2000, April 2001
	Vegetable	30	August 1998, November 1998, May 1999, August 1999, March 2000
Control	Water	25	February 2001
	Soil	6	April 2000, February 2001
	Paddy	3	February 2001
	Vegetable	3	February 2001

* Although I had collected some samples in the months of February and April 2001

Instrumental Techniques

The FI-HG-AAS was used in School of Environmental Studies (SOES), Jadavpur University, Kolkata, India

A flow injection-hydride generation - atomic absorption spectrometry (FI-HG-AAS) technique was used in our laboratory for analysis of total arsenic in water, soil, crop, and vegetable samples. The FI-HG-AAS system was assembled from commercially available instruments and accessories in our laboratory. A Perkin-Elmer Model 3100 spectrometer equipped with a Hewlett-Packard Vectra computer with GEM software, Perkin-Elmer EDL System-2, arsenic lamp (lamp current 400 mA), and Varian AAS Model Spectra AA-20 with hollow-cathode As lamp (lamp current 10 mA) were used. The flow injection assembly consists of an injector, Teflon T-piece, tigon tubing and other parts for the FI system from Omni-fit UK. The peristaltic pump (VGA-76) from Varian and Minipuls-3, Gilson, Model M 312 (France) were incorporated into the FI system. Details of the instrumentation have been discussed in our earlier publications[3,4]. A Heraeus muffle furnace fitted with manual temperature control was used for dry ashing.

The ICP-MS was used in National Institute of Health Sciences (NIHS), Tokyo, Japan

A microwave digestion system (MDS-2100) from CEM Innovators in Microwave Technology, USA with a rotor for twelve Teflon digestion vessels HP-500, was used for sample digestion using HNO_3 and H_2O_2.

The ICP-MS was used from Department of Environmental Chemistry, National Institute of Health Sciences, Tokyo, Japan. Estimation of arsenic and other metals and metalloids in soil, vegetable, and paddy, (rice & husk) have been carried out by ICP-MS method. Analytical results of SRM digested similarly and analyzed by ICP-MS. The instrumental conditions of this system are shown in Table 6.

Table 6: Instrumental conditions for ICP-MS

Mobile phase	**Milli-Q** water
Flow rate	1mL/min
Infection volume	20 µL
Radio frequency(RF)	1300W
RF refracting power	Below 5W
Flow of plasma gas	15 L/min
Flow of Carrier gas	1.2 L /min
Measuring time	2 min
Peristaltic pump	0.2 rps
Spray chamber temp.	2°c

The IC-ICP-MS was used from Department of U.S. Food & Drug Administration, Forensic Chemistry Center, Cincinnati, USA.

The IC-ICP-MS was used from Department of U.S. Food and Drug Administration (FDA), Forensic Chemistry Center, Cincinnati, USA. The chromatographic system used consisted of a model GP 50 ion chromatography pump (Dionex, Sunnyvale, CA, USA), AS 3500 autosampler (Thermo Separations Products, San Jose, CA, USA) and a non-metallic automated switching valve (Waters, Milford, MA, USA) with 20 µL injection loop between the Column outlet and ICP-MS nebulizer. Operation of the valve was controlled using signal relays from the IC pump.

A model PQ3 ICP-MS (VG Elemental) operating under normal multi-element tuning condition was used for chromatographic detection. Column effluent was directed to the concentric nebulizer and cooled conical spray chamber of the ICP-MS using a length (~60 em) of 0.25 mm. i.d. PEEK® tubing. An anion exchange column, Hamilton PRP-X 100 (4.6 x 150 mm), was used for separation of arsenic species.

Chemicals and Reagents

School of Environmental Studies, Jadavpur University, West Bengal, India

All reagents were of analytical grade. Distilled demonized water was used throughout. Standard arsenic solutions were prepared by dissolving appropriate amounts of As_2O_3 (Merck, Germany) and standard arsenic (V) Titrisol (Merck, Germany). Standard stock solutions were stored in glass bottles and kept refrigerated. Dilute arsenic solutions for analysis were prepared daily. The reducing solution was sodium tetrahydroborate (Merck, Germany) 1.5% (m/v) in 0.5% (m/v) sodium hydroxide (E. Merck, India Limited). The HCl (E. Merck, India Limited) concentration was 5M. Ashing acid suspension was prepared by stirring 10% (w/v) $Mg(NO_3)_2$. $6H_2O$ and 1% (w/v) MgO in water until homogeneous[4].

Standard reference materials were used to check the accuracy of the method. Pond Sediment NIES- 2, from the National Institute for Environmental Studies, Japan; Standard Chinese River Sediment 81-101 (of 1981); San Joaquin Soil SRM 2709, Citrus Leaves SRM 1572, Rice Flour SRM 1568a, Spinach Leaves SRM 1570a and Tomato Leaves SRM 1573a are from the National Institute of Standards and Technology (NIST), USA.

In National Institute of Health Sciences, Tokyo, Japan

All reagents were of analytical reagent grade. Milli-Q Water (Yamato Millipore filter, WT 100) was used throughout. Stock solutions (10 mg/L in water) of arsenic and other elements (Se, Cu, Zn, Pb, Mn, Ni, Hg) were prepared separately from 1000 mg/L stock standard (Cica-Merck, Kanta Chemical Co. Inc, Japan) of each element. All stock solutions were stored in polyethylene bottles and kept at 4°C. Dilute solutions (2.5, 5, 10, 20, 30, and 50 µg As/L) for analysis were prepared daily.

The samples digestion was carried out with concentrated nitric acid (HNO_3) (Wako Pure Chemical Industries Ltd., Osaka, Japan) and high purity hydrogen peroxide (H_2O_2) (Wako Pure Chemical Industries Ltd., Osaka, Japan).

Standard reference materials were used to check the accuracy of the method for multi element analysis. Rice flour SRM 1568a, Apple leaves SRM 1515, Tomato Leaves SRM 1573a, San Joaquin Soil SRM 2709, and Spinach leaves SRM 1570a are from the National Institute of Standards and Technology (NIST), USA.

In U.S. Food and Drug Administration, Cincinnati, U.S.A.

Ultrapure deionized water was used (DIW, Millipore, MA, USA). High-purity ammonium hydroxide was from Fisher Scientific (Fair Lawn, NJ, USA). Anhydrous trifluoroacetic acid (TFA) was from Sigma (St. Louis, MO, USA), and ammonium nitrate, and monobasic ammonium phosphate were from J.T. Baker (Phillipsburg, NJ, USA).

Commercial stock standards of As(III) and As(V) (1000 µg As/mL as As_2O_3 in 2% HCl and H_3AsO_4. ½ H_2O in 2% HNO_3, respectively) were obtained from Spex Industries (Metuchen, NJ, USA). Dimethylarsinic acid (98.0%) and disodium methyl arsenate (99%) were obtained from Chem Service (West Chester, PA, USA). The mobile phase consisted of 10 mM $NH_4H_2PO_4$ and 10 mM NH_4PO_3 adjusted to a pH of 6.3 with NH_4OH. NIST SRM 1568a rice flour was used for method validation

Sample collection and preservation

Water samples

Tube well water samples were collected in pre-washed (with 1:1 HNO_3) polyethylene bottles. After collection concentrated nitric acid (1.0 ml per liter) was added as preservative. Samples, which were not analyzed immediately, were kept in a refrigerator at 4°C. Details of the collection procedure have been described in our earlier publications[3,4].

Vegetable and crop samples

Vegetable and crop samples were collected from selected agricultural fields where arsenic contaminated water was used for agricultural purposes. Vegetable, crop, and plant samples were picked by hand, stored in polyethylene bags, and kept cool until processing in the lab. Samples were washed thoroughly with tap water to remove soil and other particles, and finally washed in sonicator with demonized water for several times. Prior to sample washing, plants consisting of both roots (below soil surface) and shoots (above soil surface) were separated into root, stem, leaf, and fruit as a sub samples and dry matter yields after drying at 60°C for about 72 hours. Dry samples made fine powder by Agate pestle and mortar, sieved, and stored in polyethylene bags with proper leveling at room temperature.

Soil samples

Surface soil samples and samples at different depth were collected from agricultural fields, where arsenic contaminated water was used for agricultural purposes and samples were also collected from non-arsenic contaminated agricultural fields (arsenic concentration in agricultural water was <3 µg/L). We collected four soil samples from different part of the same field and made a mixture. Samples were picked by non-metallic spoon, stored in polyethylene bags, and kept cool until processing in the lab. First soil samples were dried at room temperature and finally at 60°C for several hours. Dried samples were made fine powder by Agate pestle and mortar, sieved, and stored in polyethylene bags with proper leveling at room temperature.

Sample treatment for analysis

In SOES Laboratory

Sand bath digestion of soil samples

Approximately 0.10 to 0.50 gm of soil sample was placed in a 25cc conical flask (glass), 2 mL deionized water added, followed by 2 mL concentrated HNO_3 and 1 mL concentrated H_2SO_4 (Analar Grade, E. Merck, India). The mouth of the flask was covered with a small glass funnel. Then it was heated on a sand bath until the fumes of SO_3 evolved. When fumes of SO_3 evolved, heating was discontinued and after cooling, the solution was diluted and filtered through a millipore membrane (0.45µm pore size) filtering apparatus, then adjusted to fixed volume. Standard Reference Materials (SRM) was analyzed in the same way to test the accuracy.

Dry ashing digestion of vegetable and crop samples

Approximately 0.20 to 0.70 gm of dry vegetable/ crop sample or 1.5 gm to 3.0 gm of wet/weight vegetable sample was taken into a 100 ml Borosil Conical Flask and 10 ml ashing aid [10% (w/v) $Mg(NO_3)_2$. $6H_2O$ (Riedel-De Haenag, Seelze-Hannover, Germany) + 1% (w/v) MgO (E. Merck, Darmstadt, Germany) in deionized water] was added with continuous agitation. Then 5 mL HNO_3 (40%, v/v) was added and evaporated to almost dryness on a hot plate at about 90-100°C. When the sample dried, the beakers were covered with a pre-washed watch glass and transferred to the muffle furnace[2].

The following temperature program was adopted for proper ashing of the sample: 150°C for l hr, 200°C for 30 min, 250°C for 30 min, 300°C for 2 hrs, 400°C for l hr, and 450°C for 12-14 hrs. After cooling to room temperature 2 mL (10% v/v) HNO_3 was added to the carbonaceous residue. The mixture was dried again on the hot plate to dryness and transferred to the furnace. The ash was subjected again to the following temperature program: 150°C for 1 hr and 30 min, 300°C for 30 min, and 450°C for 12- 14hrs. After cooling the white ash was moistened with a few drops of water, dissolved in 1-2 mL 6M HCI and filtered through a Millipore filter (0.45 µm) and finally made the proper volume with 6M HCl. Triplicate blanks and Standard Reference Materials (SRM) were-prepared following the same digestion procedure.

Microwave digestion of soil, vegetable, and crop samples in NIHS, Tokyo, Japan

Samples for digestion were weighed (0.2 gm to 0.5 gm of dry sample) in the Teflon vessel and added 2:1 v/v of nitric acid and hydrogen peroxide. The vessels were closed using the lid provided. For safety of the vessel, rupture membrane was inserted in the lid. Vessels were set in the turn table of the micro-wave digestion machine and the below settings were programmed(Table7). After cooling for 30 minutes, the vessels were opened carefully. Each digested solution was transferred quantitatively to a 10 mL volumetric flask and adjust to fixed volume with Milli-Q water. Finally, it was filtered through a Millipore membrane (0.45 µm) (CASL 45 2.5 CMD, membrane: Acetyl Cellulose) and kept in plastic container for analysis. The Standard Reference

Table 7: Optimum parameters for sample digestion by microwave system

Stages	1	2	3	4	5
Power(watt)	80	80	80	0	0
PSI	70	120	170	20	20
Time(min)	20	20	20	20	20
TAP(min)	5	5	5	5	0000

Materials (SRM) were digested under the same digestion procedure.

Preparation and extraction of crop and vegetable samples for arsenic speciation (FDA lab, USA)

The rice and vegetable samples were grounded in an acid-washed glass mortar and pestle. A larger amount of each of the paddy sample was shipped; therefore, they were milled and sieved (0.5 mm) in a model ZM100 ultra-centrifugal mill (Retsch, Haan Germany). Prepared samples we restored in HDPE bottles at ambient temperature prior to use.

Sample (0.1-0.5gm) were mixed with 0.5-2 mL of 2M trifluoroacetic acid (TFA) and allowed to stand for 6 hours at 100°C in either a 15 mL or a 60 mL capped HDPE centrifuge tube. The TFA extract was allowed to cool and diluted to volume (10-25 ml) with Ultrapure deionized water (DIW, Millipore, MA, USA). Extracts were filtered through a 0.45 µm Nylon syringe filter prior to analysis by IC-ICP-MS.

Sample analysis

Flow injection-hydride generation-atomic absorption spectrometry (FI-HG-AAS) (SOES Lab.)

The sample was injected into a carrier stream of 5M HCl by means of a six-port sample injection valve fitted with a 50 µL sample loop. The injected sample, together with carrier solution met subsequently with a continuous stream of sodium tetrahydroborate. Mixing with sodium tetrahydroborate generated hydride, which subsequently entered the ice water bath and then the gas-liquid separator apparatus, which was cooled with ice-cold water. This cooling procedure and the design of the gas-liquid separator are more efficient than conventional FI-AAS and the possibility of water vapor entering the quartz cell is reduced to a great extent. Inside this apparatus a continuous flow of N_2 carrier gas assists mixing and the reaction and subsequently carries hydride to the quartz tube mounted in the air-acetylene flame for As measurement. Peak signals were recorded using a computer linked to the atomic absorption spectrophotometer (AAS) that is capable of both peak height and peak area measurement. The peak height signals were measured and the concentrations of arsenic of the samples were measured/calculated against the standard curve. The experimental condition for FI-HG-AAS system is given inthe Table 8.

Table 8: Optimum-Parameters for arsenic determination by flow infection (FI) system

Parameters	Perkin-Elmer (Model 3100)	Varian (Model Spectra AA-20)
Lamp Current	400mA (EDL power supply)	10mA (hollow cathode)
Wave length	193.7 nm	193.7 nm
Slit	0.7 nm	0.5 nm
HCl flow rate	1.25 mL/min	1 mL/min
HCl concentration	5M	5M
$NaBH_4$ flow rate	2 mL/min	1.5 mL/min
$NaBH_4$ concentration	1.5% (w/v) in 0.5% (w/v) NaOH solution	1.5% (w/v) in 0.5% (w/v) NaOH solution
Carriergas	Nitrogen	Nitrogen
Carrier gas flow rate	130 mL/min	50 mL/min
Flame	Air-acetylene	Air-Acetylene

Water Samples

Preserved water samples (in 1 mL HNO_3 per liter of water) were analyzed by FI-HG-AAS against arsenite and arsenate mixture (1:1) as the standard.

Soil, vegetable, and crop samples

Digested samples were analyzed by Fl-HG-AAS method against arsenate as the standard.

Inductively Coupled Plasma-Mass Spectrophotometry (ICP-MS) (NIHS Lab, Japan)

ICP-MS Analysis

ICP-MS is an element selective detector. Twenty microliters (20 µL) of the microwave acid digested sample were injected into a carrier stream of Milli-Q water with a sample loop. The Chromatographic areas were measured, and the concentrations of elements were calculated against the individual element standard curve. The experimental conditions of ICP-MS are given in Table 6**.**

Ion chromatography-inductively coupled plasma-Mass spectrophotometry (IC-ICP-MS) (FDA Lab, USA)

Figure 7 shows the chromatogram obtained for a standard mixture of As(III), DMA, MMA and As(V) in our experimental condition (Table 9). Each of the arsenic species is present at an arsenic concentration of 2 ng/mL. Data was collected for 10 minutes. The four arsenic species are baseline resolved in under 8.5 minutes; however, arsenobetaine (AsB) is not resolved from As(III) under these separation conditions. AsB is generally found in fish and shellfish samples and is not expected to be present in vegetable or rice samples collected from arsenic contaminated agricultural fields. The precision of peak areas measured over a period of 4 hours (n=5) using replicate 25 µL injections of a standard containing 2 ng/mL each of As(III), DMA, MMA and As(V) was 4.8%, 4.4%, 4.1%, and 9.0%, respectively. As estimate of the instrumental detection limit (IDL) for each of the arsenic species was calculated based on 3 times, the standard deviation of peak area measurements for replicate 25 µl injections of a standard containing 0.2 ng As/mL each of As(III), DMA, MMA and As(V). The IDLs were 0.1, 0.1, 0.1 and 0.2 ng/mL for As(III), DMA, MMA and As(V), respectively.

Table 9. IC-ICP-MS operational condition

Column	Ananion exchange column, Hamilton PRP-X100 (4.6x150 mm)
Mobile phase	10 mM $NH4H_2PO_4$, 10 mM NH_4NO_3 adjusted to a pH of 6.3 with NH_4OH
Flow rate	1mL/min
Sample volume	20 µL
Detector	ICP-MS
Forward Power	1350 w
Coolant Ar flow	12 L/min
Auxiliary Ar flow	1.0 L/min
Nebulizer flow	0.8 L/min
Monitoring mass	m/z 75
Sample rate	0.5 Hz
Elution order of Arsenic species	As(III), DMA, MMA, As(V)

Samples were analyzed using calibration standards at 0.5, 1, 2, 5 and 10 ng/mL concentrations (in some cases a 20 ng/mL standard was also used). Peak areas were corrected for any drift associated with the flow injection signal at the beginning of each chromatogram. The concentrations of several samples were also checked using standard addition.

Spikes of each of the arsenic species were taken through the method and spike recoveries of 83%, 88%, 100%, and 93% were obtained for As(III), As(V), MMA and DMA respectively. However. it should be noted that As(V) can be partially reduced during the extraction procedure. The As(V) recovery was calculated in spiked samples using the sum of the increase in the As(III) and As(V) concentrations. Because of this partial reduction, the method is only capable of providing total inorganic arsenic as the sum of the As(III) and As(V) concentrations. Standard NIST SRM 1568a Rice Flour also analyzed by the same procedure and the sum of the arsenic species concentrations for SRM Rice Flour (0.27 µg/gm) compared well with the certified total arsenic value (0.29 µg/gm).

Total arsenic in irrigation tubewells, soil, vegetable, paddy samples were analyzed by using FI-HG-AAS after dry ashing (vegetable, rice, and husk) and acid digestion (soil)

Water samples used for cultivation had been collected from 10 locations and analyzed by FI-HG-AAS method and their results are given in Table 10. Similarly, soil samples had

Table 10: Analysis of arsenic and iron for 10 irrigation tube-well

Tube wellNo.	August1998		November1998		May1999		February2000		April2000		April2001	
	As (µg/L)	Fe (µg/L)	As (µg/L)	Fe (µg/L)	As (µg/L)	Fe (µg/L)	As (µg/L)	Fe (µg/L)	As (µg/L)	Fe (µg/L)	As (µg/L)	Fe (µg/L)
F-TW1	700	4875	-	-	724	4833	789	5025	805	5358	827	5850
F-TW2	560	5897	540	6792	579	6999	560	6852	570	6958	589	7600
F-TW3	110	3325	103	3126	125	3602	135	3249	156	3927	145	3560
F-TW4	460	7354	-	-	468	6862	455	7187	488	7771	475	7910
F-TW5	355	5250	-	-	398	5027	452	4760	477	5180	496	5580
F-TW6	200	4850	210	3951	215	4326	-	-	-	-	185	4180
F-TW7	215	4425	-	-	-	-	228	5292	218	4720	238	4870
F-TW8	220	4110	208	3680	215	3950	218	4420	233	4720	217	4900
F-TW9	220	3860	-	-	-	-	-	-	240	4220	-	-
F-TW10	135	2562	-	-	140	2979	151	3200	195	3229	176	3140

Table 11: Analysis of arsenic in soil where arsenic contaminated groundwater was used for cultivation

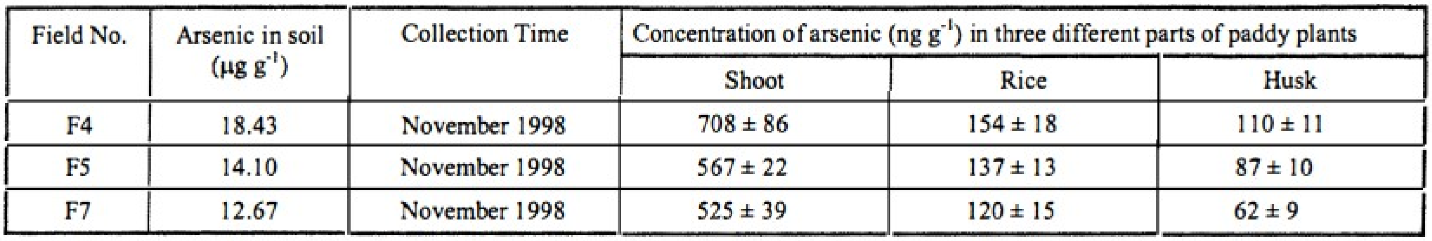
Field No.	Average As concentration in water over 21 months ($\mu g\ l^{-1}$)	Average Fe concentration in water over 21 months ($\mu g\ l^{-1}$)	August 1998 As in $\mu g\ g^{-1}$	November 1998 As in $\mu g\ g^{-1}$	May 1999 As in $\mu g\ g^{-1}$	August 1999 As in $\mu g\ g^{-1}$	February 2000 As in $\mu g\ g^{-1}$	April 2000 As in $\mu g\ g^{-1}$	April 2001 As in $\mu g\ g^{-1}$
F1	769	5188	23.27	15.67	28.15	20.62	28.73	34.15	18.76
F2	566	6949	29.32	18.37	29.96	25.14	36.37	43.08	17.97
F3	129	3375	10.81	14.96	14.20	16.27	15.37	17.46	11.23
F4	469	7417	27.73	18.43	30.90	30.26	28.87	34.11	28.69
F5	436	5159	25.37	14.10	35.92	31.26	32.72	31.95	24.83
F6	202	4326	17.31	14.38	16.44	22.77	18.62	25.63	19.97
F7	225	4826	22.11	12.67	24.02	23.23	23.58	25.54	22.35
F8	218	4296	22.20	13.82	-	20.07	21.89	22.32	7.91
F9	230	4090	23.21	11.87	20.02	22.32	21.20	23.67	8.32
F10	159	3022	22.25	18.29	16.62		24.96	23.41	18.62

Table 12: Distribution of arsenic concentration in different parts of the vegetable collected from 6 fields out of 10 irrigated with arsenic contaminated water

Field No.	Arsenic concentration in water ($\mu g\ l^{-1}$) *	Arsenic concentration in soil ($\mu g\ g^{-1}$)	Type of the sample / plant name	Collection time/ month	Arsenic concentration in ng g^{-1}			Fruit (dry) (ng g^{-1})	Skin (dry) (ng g^{-1})
					Stem (dry)	Leaf (dry)	Fruit (wet/weight)		
F4	355	18.43	Spell	November 98	320 ± 15	410 ± 20	28 ± 3	-	-
F2	560	29.32	Spell	August 98	478 ± 12	630 ± 40	38 ± 6	-	-
F6	200	17.31	Spell	August 98	253 ± 15	344 ± 21	13 ± 2	-	-
F5	460	25.37	Spell	August 98	390 ± 16	490 ± 22	26 ± 5	-	-
F8	210	-	Spell	May 99	182 ± 6	214 ± 15	22 ± 5	-	-
F10	140	16.62	Spell	May 99	136 ± 14	173 ± 11	9 ± 2	48 ± 7	-
F4	460	18.43	Egg plant	November 98	230 ± 12	286 ± 14	23 ± 4	225 ± 16	420 ± 25
F5	355	14.10	Egg plant	November 98	235 ± 15	324 ± 25	28 ± 3	253 ± 21	-
F1	720	28.15	Egg plant	May 99	432 ± 33	525 ± 22	60 ± 4	-	-
F2	579	25.14	Egg plant	August 99	360 ± 12	413	49 ± 8	443 ± 33	-
F8	215	20.07	Egg plant	August 99	267 ± 12	288 ± 14	25 ± 5	227 ± 17	405 ± 21
F3	125	16.27	Lady's Finger	August 99	45± 3	61± 7	11 ± 3	65 ± 8	-
F2	565	29.96	Lady's Finger	May 99	198 ± 12	239± 13	21 ± 3	135 ± 15	289 ± 21
F6	215	22.77	Lady's Finger	August 99	192 ± 10	218 ± 8	17 ± 2	-	-

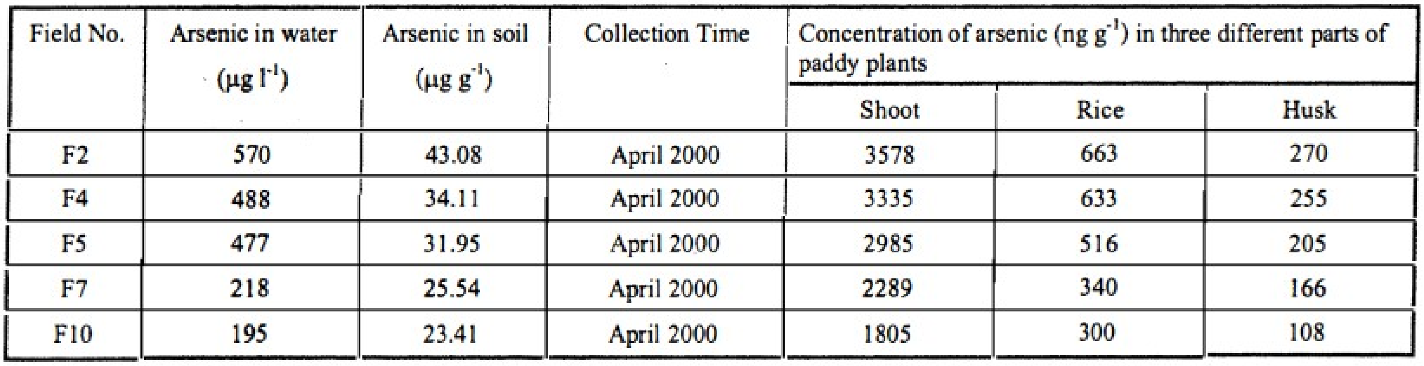
* Arsenic concentration when samples were collected

Table 13: Distribution of arsenic concentration in different parts of paddy plant collected from 3 selected location of Kolsur (N) in Deganga block, North 24-Parganas, West Bengal, India during monsoon period and rainwater was used for cultivation



Field No.	Arsenic in soil ($\mu g\ g^{-1}$)	Collection Time	Concentration of arsenic ($ng\ g^{-1}$) in three different parts of paddy plants		
			Shoot	Rice	Husk
F4	18.43	November 1998	708 ± 86	154 ± 18	110 ± 11
F5	14.10	November 1998	567 ± 22	137 ± 13	87 ± 10
F7	12.67	November 1998	525 ± 39	120 ± 15	62 ± 9

Table 14: Distribution of arsenic concentration in different parts of paddy plant collected from 5 selected fields of Kolsur (N) village in Deganga block, North 24-Parganas, West Bengal, India during pre-monsoon period and cultivated with arsenic contaminated groundwater



Field No.	Arsenic in water ($\mu g\ l^{-1}$)	Arsenic in soil ($\mu g\ g^{-1}$)	Collection Time	Concentration of arsenic ($ng\ g^{-1}$) in three different parts of paddy plants		
				Shoot	Rice	Husk
F2	570	43.08	April 2000	3578	663	270
F4	488	34.11	April 2000	3335	633	255
F5	477	31.95	April 2000	2985	516	205
F7	218	25.54	April 2000	2289	340	166
F10	195	23.41	April 2000	1805	300	108

Table 15: Analytical results of Standard Reference Matarial (SRM) by FI-HG-AAS

Sample	Certified value	Found value
NIST,SRM1572(CitrusLeves)	3.1± 0.3(µg/gm)	3.5± 0.5(µg/gm)
NIES-2(PoundSediment)	12.2±2(µg/gm)	9.85 ±0.5(µg/gm)
ChinesRiverSediment81-101(of1981)	56.0±10.0(µg/gm)	53.79±2.0 (µg/gm)
NIST,SRM2709(SanJoaquinSoil)	17.7±0.8(µg/gm)	16.87±0.34(µg/gm)
NIST,SRM®1568a(RiceFlour)	0.29 ±0.03(µg/gm)	0.28±0.04(µg/gm)
NIST,SRM157 0$_8$(SpinachLeaves)	0.068±0,012(µg/gm)	0.062±0.014(µg/gm)
NIST,SRM1573a(TomatoLeaves)	0.112±0.004(µg/gm)	0.100(µg/gm)

Arsenic concentration in irrigation tube well and soil before and after a devastating flood

During September 2000 to October 2000 of our 10 experimental Fields were submerged with water due to a devastating flood. The analytical results are given in Table 16.

Table 16: Arsenic concentration in irrigation tube well and soil before and after a devastating flood

Tubewell No./Field No.	Arsenic concentration in water (µg/L)		Arsenic concentration in soil (µg/g)	
	Before flood (April 2000)	After flood (April 2001)	Before flood (April 2000)	After flood (April 2001)

FTW1/Fl	805	827	34.15	18.76
FTW2/F2	570	589	43.08	17.97
FTW3/F3	156	145	17.46	11.23
FTW4/F4	488	475	34.11	28.69
FTW5/F5	477	496	31.95	24.83
FTW6/F6	-	185	25.63	19.97
FTW7/F7	218	238	25.54	22.35
FTW8/F8	233	217	22.32	7.91
FTW9/F9	240	-	23.67	8.32
FTW10/FI0	195	176	23.41	18.62

been collected from 10 fields where contaminated underground water was used for cultivation. The analytical results of those soil samples are given in Table 11. Vegetable and paddy samples (including various parts) cultivated with arsenic contaminated water had been collected time to time from selected fields. Their analytical results are given in Table 12, 13, & 14, respectively. Analytical results of Standard Reference Material (SRM) digested similarly & analyzed by FI-HG-AAS given in Table 15.

Total arsenic and other metals and metalloids in soil, vegetables, and paddy (rice & husk) samples by using ICP-MS after microwave digestion.

Estimation of arsenic and other metals and metalloids in soil, vegetable, and paddy, (rice & husk) have been carried out by ICP-MS method. Total arsenic and other metals and metalloids concentration in soil, rice (also in husk) and vegetable are given in Table 17, 18, and 19 respectively. Analytical results of SRM digested similarly and analyzed by ICP-MS given in Table 20.

Table 17: Concentration (µg/gm) of 7 elements in 9 contaminated soils collected from arsenic contaminated fields of West Bengal, India and Bangladesh

FieldNo.	Asinwater(µgrl)	Typeofsample	As	Mn	Cu	Hg	Pb	Ni	Zn
Fl	805	Soil	34.15	732.9	58..44	1.13	67.36	72.29	80.38
F2	570	Soil	43.08	508.20	49.07	1.13	52.87	53.76	105.00
F3	156	Soil	17.46	388.33	38.25	1.36	39.67	40.48	58.53
F4	488	Soil	34.11	538.68	54.65	1.20	52.38	53.71	70.08
F6	215	Soil	25.63	514.93	49.16	1.26	57.12	61.44	68.54
F7	218	Soil	25.54	457.46	46.34	1.47	40.33	51.12	45.62
Fl0	195	Soil	23.41	415.47	42.60	1.61	43.87	44.59	52.12
Bangladesh	492	Soil	40.98	484.29	51.05	1.15	46.89	50.08	-
Bangladesh	525	Soil	42.13	473.62	49.20	0.96	55.92	61.67	71.47

Table18: Concentration (µg/gm) of 7 elements in rice and husk collected from arsenic contaminated agricultural fields of West Bengal-India and Bangladesh

Field No.	Arsenic in water (µg/L)	Arsenic in soil (µg/gm)	Sample type	Elements						
				As	Se	Mn	Cu	Hg	Pb	Ni

Bangladesh	205	18.77	Rice	0.273	0.458	25.63	5.705	0.086	0.154	0.925
			Husk	0.067	0.020	27.84	0.785	0.112	0.130	0.598
F2	570	43.08	Rice	0.749	0.280	22.09	7.61	0.085	0.027	0.090
			Husk	0.318	0.003	27.22	1.465	0.113	0.216	0.187
F4	488	34.11	Rice	0.780	0.262	22.64	7.61	0.086	0.037	1.19
			Husk	0.308	BDL	30.98	1.662	0.123	0.087	1.281

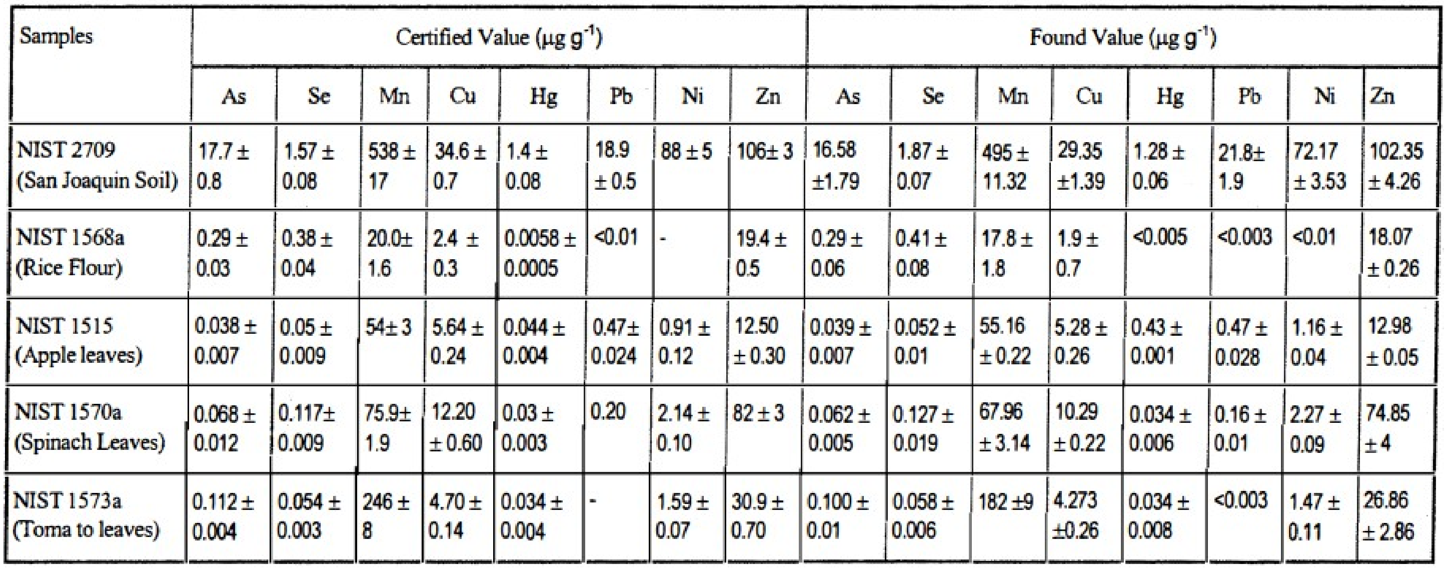
BDL:BelowDetectionLimit

Table 19: Concentration (µg/gm) of 7 elements in vegetable samples collected from arsenic contaminated agricultural fields of Bangladesh

Field	Arsenic in water (µg/L)	Type of sample	Elements						
			As	Se	Mn	Cu	Hg	Pb	Ni
Bangladesh	205	Data*(Stempart)	0.043	0.420	511.97	50.25	0.674	1.98	31.47
Bangladesh	205	**Root part of an esculent edible plant	0.729	0.255	113.35	22.32	0.513	0.236	4.21

*A kind of vegetable, whole portion (stem+leaf) is used for food and local name 'Data'
**A kind of popular vegetable, whole portion (root+stem+leaf) is used for food and local name 'Kachu'.

Table20:Analytical results of NIST Standard Reference Material (SRM) by ICP-MS



Samples	Certified Value (µg g^{-1})								Found Value (µg g^{-1})							
	As	Se	Mn	Cu	Hg	Pb	Ni	Zn	As	Se	Mn	Cu	Hg	Pb	Ni	Zn
NIST 2709 (San Joaquin Soil)	17.7 ± 0.8	1.57 ± 0.08	538 ± 17	34.6 ± 0.7	1.4 ± 0.08	18.9 ± 0.5	88 ± 5	106± 3	16.58 ±1.79	1.87 ± 0.07	495 ± 11.32	29.35 ±1.39	1.28 ± 0.06	21.8± 1.9	72.17 ± 3.53	102.35 ± 4.26
NIST 1568a (Rice Flour)	0.29 ± 0.03	0.38 ± 0.04	20.0± 1.6	2.4 ± 0.3	0.0058 ± 0.0005	<0.01	-	19.4 ± 0.5	0.29 ± 0.06	0.41 ± 0.08	17.8 ± 1.8	1.9 ± 0.7	<0.005	<0.003	<0.01	18.07 ± 0.26
NIST 1515 (Apple leaves)	0.038 ± 0.007	0.05 ± 0.009	54± 3	5.64 ± 0.24	0.044 ± 0.004	0.47± 0.024	0.91 ± 0.12	12.50 ± 0.30	0.039 ± 0.007	0.052 ± 0.01	55.16 ± 0.22	5.28 ± 0.26	0.43 ± 0.001	0.47 ± 0.028	1.16 ± 0.04	12.98 ± 0.05
NIST 1570a (Spinach Leaves)	0.068 ± 0.012	0.117± 0.009	75.9± 1.9	12.20 ± 0.60	0.03 ± 0.003	0.20	2.14 ± 0.10	82 ± 3	0.062 ± 0.005	0.127 ± 0.019	67.96 ± 3.14	10.29 ± 0.22	0.034 ± 0.006	0.16 ± 0.01	2.27 ± 0.09	74.85 ± 4
NIST 1573a (Toma to leaves)	0.112 ± 0.004	0.054 ± 0.003	246 ± 8	4.70 ± 0.14	0.034 ± 0.004	-	1.59 ± 0.07	30.9 ± 0.70	0.100 ± 0.01	0.058 ± 0.006	182 ±9	4.273 ±0.26	0.034 ± 0.008	<0.003	1.47 ± 0.11	26.86 ± 2.86

Arsenic species in paddy (rice+ husk), rice, husk, and vegetable by IC-ICP-MS after TFA (trifluoroacetic acid) extraction

The analytical results are given in Tables 21 and 22.

Table 21: Concentration of arsenic species (ng/gm) and percentage of inorganic arsenic and methylated arsenic in rice, husk, paddy (rice+ husk) & vegetable (dry) collected from arsenic contaminated fields in Kolsur (N) village of Deganga block, North 24-Parganas, West Bengal, India

Serial No.	Field No.	Collection month	Arsenic in irrigated water ($\mu g\ l^{-1}$)	Arsenic in soil ($\mu g\ g^{-1}$)	Type of sample	Inorganic arsenic [As(III)+As(V)] ($ng\ g^{-1}$)	Methylated Arsenic		Sum of As species ($ng\ g^{-1}$)	Percentage (%) of arsenic species	
							DMA ($ng\ g^{-1}$)	MMA ($ng\ g^{-1}$)		Inorganic [As(III)+ As(V)]	Methylated [DMA+MMA]
1	F4	November 1998	Monsoon*	18.43	Rice	114 ± 6	11 ± 2	<5	125 ± 6	91.2	8.8
2	F7	November 1998	Monsoon	12.67	Rice	89 ± 2	9 ± 1	<5	98 ± 2	90.8	9.2
3	F9	November 1998	Monsoon	11.87	Rice	49 ± 3	<5	<5	49 ± 3	100.0	
4	F5	November 1998	Monsoon	14.10	Rice	122 ± 6	<10	<10	122 ± 6	100.0	
5	F9	November 1998	Monsoon	11.87	Husk	43	<10	<10	43	100.0	
6	F4	November 1998	Monsoon	18.43	Husk	78 ± 16	<10	<10	78 ± 16	100.0	
7	F5	November 1998	Monsoon	14.10	Husk	79	<10	<10	79	100.0	
8	F7	November 1998	Monsoon	12.67	Husk	61	<10	<10	61	100.0	
9	F4	November 1998	Monsoon	18.43	Paddy	100 ± 4	8 ± 1	<5	108 ± 4	92.6	7.4
10	F5	November 1998	Monsoon	14.10	Paddy	84 ± 7	<5	<5	84 ± 7	100.0	
11	F5	April 2000	477	31.95	Paddy	380 ± 21	96 ± 6	21 ±1	497 ± 22	76.4	23.6
12	F10	April 2000	195	23.41	Paddy	234 ± 3	36 ± 4	<5	270 ± 5	86.7	13.3
13	F2	April 2000	570	43.08	Paddy	377 ± 6	136±3	<5	513 ± 7	73.5	26.5
14	F4	April 2000	488	34.11	Paddy	407 ± 8	122±5	<5	529 ± 9	76.9	23.1
15	F7	April 2000	218	25.34	Paddy	195 ± 11	13 ± 3	<5	208 ±11	93.7	6.3
16	F2	April 2000	579	25.14	Egg. Plant (fruit)	434	Trace	<5	448	96.9	3.1
17	F8	April 2000	215	20.07	Egg. Plant (fruit)	170	36	<5	206	82.5	17.5
18	F3	April 2000	125	16.27	Lady's Finger	48	10	<5	58	82.7	17.3

* In Monsoon period rainwater is used for irrigation purpose.

Table 22: Concentration of arsenic species (ng/gm) and percentage of inorg-As and methylated arsenic in paddy (rice+ husk) and vegetable (dry) collected from arsenic contaminated fields in Datterhat village of Madaripur district, Bangladesh

Serial No.	Collection month	Arsenic in irrigated water($\mu g\ l^{-1}$)	Arsenic in soil ($\mu g\ g^{-1}$)	Type of sample	Inorganic arsenic [As(III)+As(V)] ($ng\ g^{-1}$)	Methylated Arsenic		Sum of As species ($ng\ g^{-1}$)	Percentage (%) of arsenic species	
						DMA ($ng\ g^{-1}$)	MMA ($ng\ g^{-1}$)		Inorganic [As(III)+ As(V)]	Methylated [DMA+ MMA]
1B	March 2000	205	18.77	Paddy	175 ± 13	20 ± 0.6	<5	195 ± 13	89.7	10.3
2B	March 2000	185	-	Paddy	169 ± 9	22 ± 5	<5	191 ± 9	88.5	11.5
3B	March 2000	205		Bitter gourd	16 ± 3	Trace	<2	16 ± 3	100	-
4B	March 2000	205	-	Data*	36 ± 5	<2	<2	36 ± 5	100	-
5B	March 2000	205	-	Kachu (root part)**	666 ± 43	<10	<10	666 ± 43	100	-
6B	March 2000	205	-	Wheat	16 ± 3	<2	<2	16 ± 3	100	
7B	March 2000	205	-	Egg Plant (fruit)	139 ± 16	<10	<10	139 ± 16	100	-

* A kind of vegetable, whole portion (steam and leaf) is used for food and local name is 'Data'

** A kind of vegetable, whole portion (root + leaf) is used for food and local name is 'Kachu'.

Results & Discussion

Table 10 shows analysis of arsenic from August 1998 to April 2000 of 10 tube wells used in 10 fields for irrigation purpose. Although from the results of arsenic in tube wells it appears that in some of the tube wells there is increase of arsenic with time but this type of variation, we had experienced in many tube wells during our work in West Bengal-India and Bangladesh.

It has also been observed that arsenic concentration in same field varies location to location (Table 23) and concentration of arsenic is higher at the surface than at any depth (Table 24 and Figure 2). Table 24 and Figure 2 indicate that arsenic concentration is higher at surface and at depth 18-inch and 36-inch the variation is minimum.

Table 23. Distribution of arsenic concentration (µg/gm) of soil samples collected from different location of the same arsenic contaminated fields during August 1998.

	Field No. F3				Field No. F2			Field No. F6		
	Location-1	Location -2	Location -3	Location -4	Location -1	Location -2	Location -3	Location -1	Location -2	Location -3
Arsenic concentration (ug g^{-1})	13.92 ±1. 58	9.38 ± 1.63	6.29 ± 0.49	8.82 ± 1.9	24.78 ±1.78	27.84 ± 1.08	33.33 ± 2.67	13.30 ± 2.43	17.00 ± 2.15	19.65 ± 1.41

Table 24. Distribution of arsenic concentration (µg/ gm) in contaminated soil with depth

Field No.	Surface soil arsenic concentration in µg g^{-1}	18 inch depth arsenic concentration in µg g^{-1}	36 inch depth arsenic concentration in µg g^{-1}
F1	18.76	9.63	8.49
F2	17.97	9.47	9.19
F3	11.23	7.38	8.06
F4	28.69	10.41	7.86
F7	22.35	12.80	12.05
F8	7.91	5.74	5.92

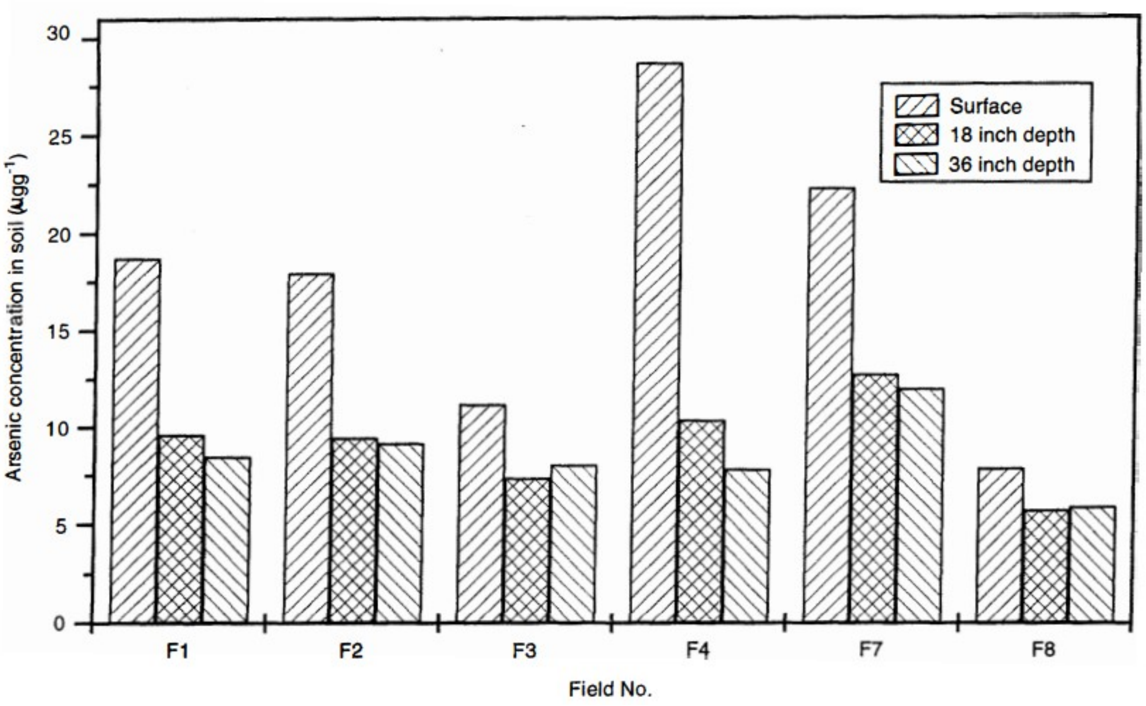
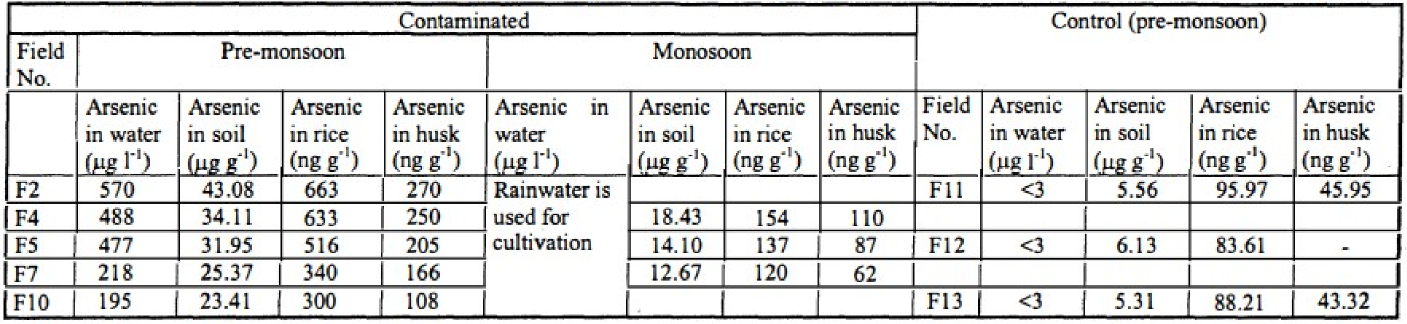


Figure 2: Distribution of arsenic concentration (µg/ gm) in soil with increasing depth (in inch.).

Table 16 shows arsenic concentration in irrigation tube wells and soil measured in April 2000 and again in April 2001 after flood. Our 21 months study on arsenic in soil, crop, and vegetable completed during April 2000. However, during September 2000 - October 2000 there was a devastating flood in West Bengal. Most of the parts of North 24-Parganas including our10 experimental fields were submerged in flood water. During April 2001 we went to the fields and collected water and soil samples from the same location of our experimental fields. Table 16 indicates that there is almost no change of arsenic in irrigation tube well, but drastic change of arsenic in soil. Thus, it appears that arsenic from soil after flood washed away but six months was not sufficient for aquifer dilution.

Table 25: Comparative study for As concentration (ng g^{-1}) in crops (rice) cultivated by using arsenic contaminated water and arsenic free water (control)



Contaminated									Control (pre-monsoon)				
Field No.	Pre-monsoon				Monosoon								
	Arsenic in water ($\mu g\ l^{-1}$)	Arsenic in soil ($\mu g\ g^{-1}$)	Arsenic in rice (ng g^{-1})	Arsenic in husk (ng g^{-1})	Arsenic in water ($\mu g\ l^{-1}$)	Arsenic in soil ($\mu g\ g^{-1}$)	Arsenic in rice (ng g^{-1})	Arsenic in husk (ng g^{-1})	Field No.	Arsenic in water ($\mu g\ l^{-1}$)	Arsenic in soil ($\mu g\ g^{-1}$)	Arsenic in rice (ng g^{-1})	Arsenic in husk (ng g^{-1})
F2	570	43.08	663	270	Rainwater is used for cultivation				F11	<3	5.56	95.97	45.95
F4	488	34.11	633	250		18.43	154	110					
F5	477	31.95	516	205		14.10	137	87	F12	<3	6.13	83.61	-
F7	218	25.37	340	166		12.67	120	62					
F10	195	23.41	300	108					F13	<3	5.31	88.21	43.32

Table 25 shows arsenic concentration in rice & husk (a) cultivated with arsenic contaminated underground water & elevated arsenic concentration in soil, (b) cultivated with rainwater & arsenic concentration in soil is low, and (c) controlled cultivation: cultivated by ground water having arsenic <3 µg/L and soil arsenic concentration 5.31-6.13 µg/gm. From the Table 25 it appears that higher the arsenic concentration in irrigation water & soil, higher is the arsenic concentration in rice & husk. In pre-monsoon cultivation paddy was grown in arsenic rich irrigated water with elevated arsenic in soil. But in monsoon cultivation, contribution of arsenic from water for irrigation was not there. So, also arsenic in soil has gone down as rainwater washed away some arsenic from soil. It shows that the average arsenic concentration in contaminated soil, rice, and vegetable were 3.81, 3.62, and 5.66 times higher than the control samples, respectively.

Estimation of arsenic in different parts of the vegetable & paddy had also been carried out to know the distribution of arsenic in stem, leaf, and fruit for vegetable and shoot, rice, & husk for paddy. Analytical results of few are represented in Tables 12-14. Table 13 is the arsenic concentration in paddy irrigated with rainwater (monsoon) and Table 14 is for paddy irrigated with arsenic contaminated groundwater (pre-monsoon).

The overall observations from Tables 12-14 are arsenic concentration in vegetable and paddy increases when arsenic in soil is higher and when cultivated with arsenic contaminated groundwater. Also, for paddy arsenic concentration decreases shoot > seed (rice) > husk and in vegetables the distribution is leaf> stem > fruit. Although it is reported[8] that root contains maximum amount of arsenic, but we could not analyze root for paddy plant as we were not sure about adhered soil remove from root. Arsenic in different parts of paddy with increasing concentration of arsenic in soil is given in Figures 3 (pre-monsoon and higher concentration of arsenic in soil) & Figure 4 (monsoon and arsenic concentration in soil is low) and that of vegetable given in Figure 5.

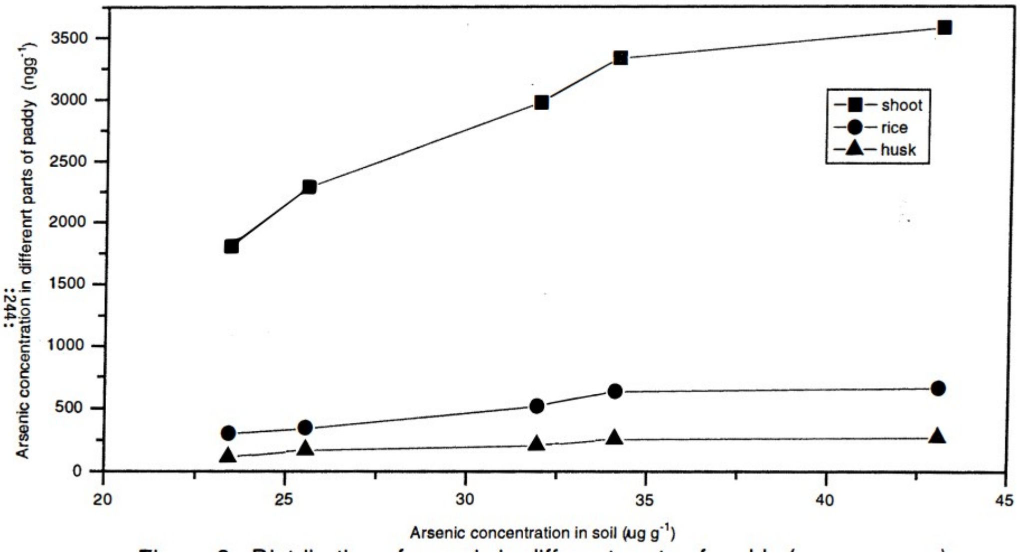


Figure 3: Distribution of arsenic in different parts of paddy (pre-monsoon) with increasing arsenic concentration in soil.

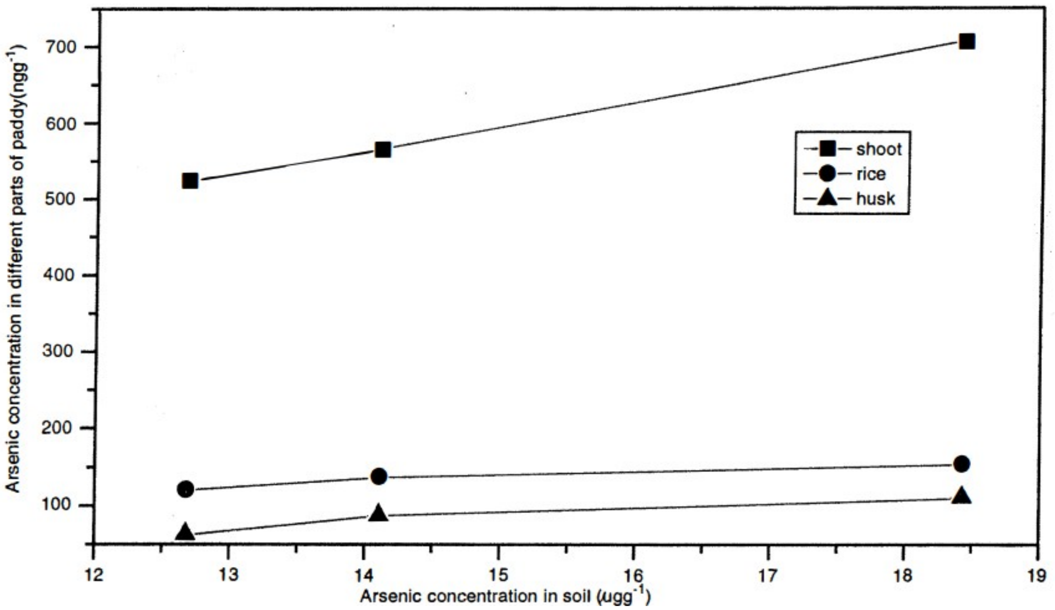


Figure 4: Distribution of arsenic concentration in different parts of paddy (monsoon) with increasing arsenic concentration in soil.

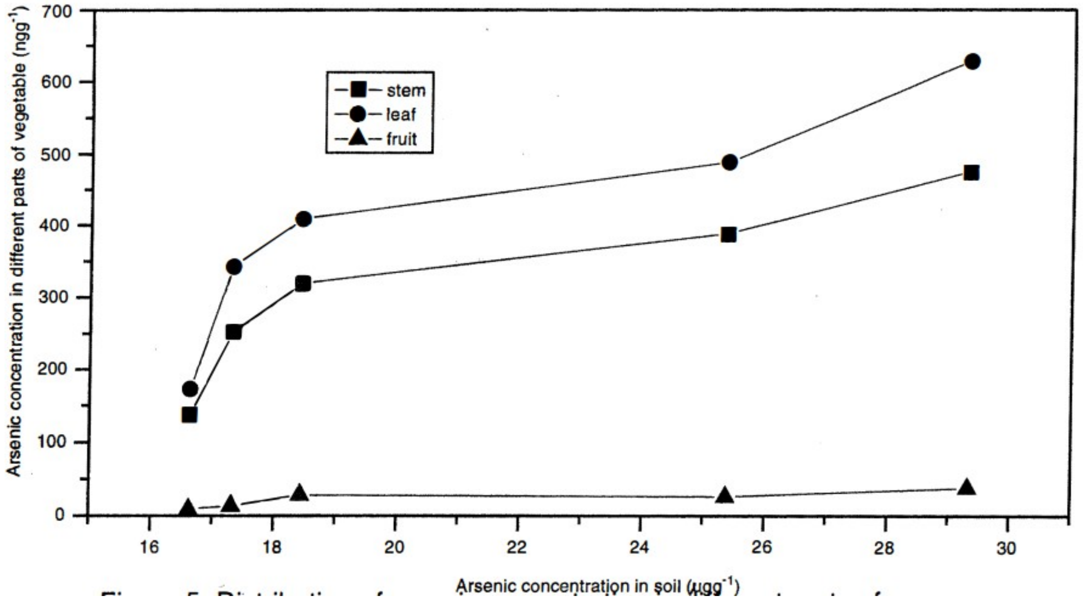


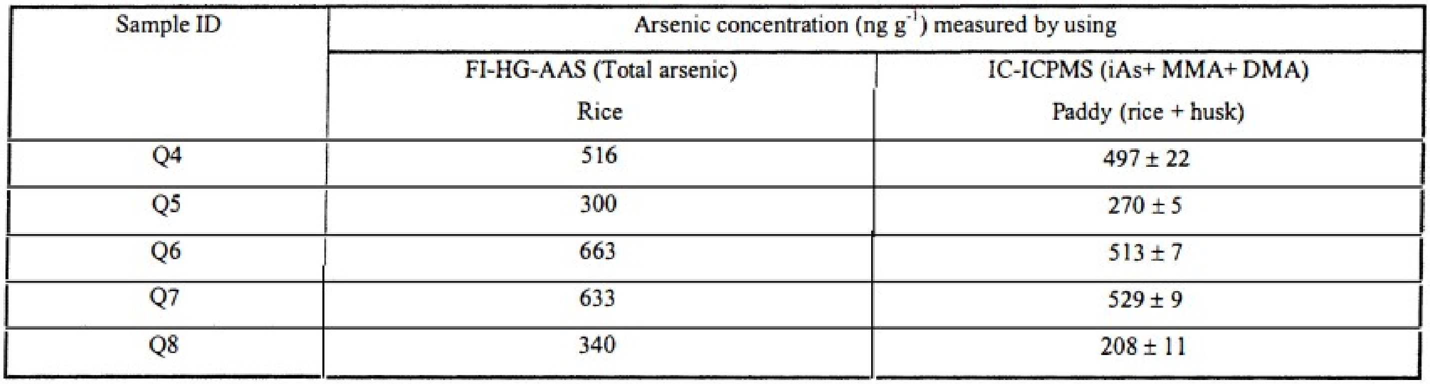
Figure 5: Distribution of arsenic concentration in different parts of vegetable with increasing arsenic concentration in soil.

Arsenic analysis of few rice and vegetable samples were done from different laboratories. Results are given in Tables 26-28. FI-HG-AAS after Teflon bomb digestion was done from SOES laboratory; microwave digestion followed by ICP-MS was done from National Institute of Health Sciences (NIHS) laboratory, Tokyo, Japan & IC-ICP-MS for various aresenic species done from US Food and Drug Administration Laboratory, Forensic Chemistry Center, Cincinnati, USA. Results of IC-ICP-MS represents only sum of inorganic arsenic (In-As) + MMA + DMA. It is expected IC- ICP-MS results will be lower compared to FI-HG-AAS & ICP-MS results after digestion.

Table 26: Arsenic concentration in same rice and paddy (rice+ husk) samples measured by using FI-HG-AAS and IC-ICP-MS in different laboratories.

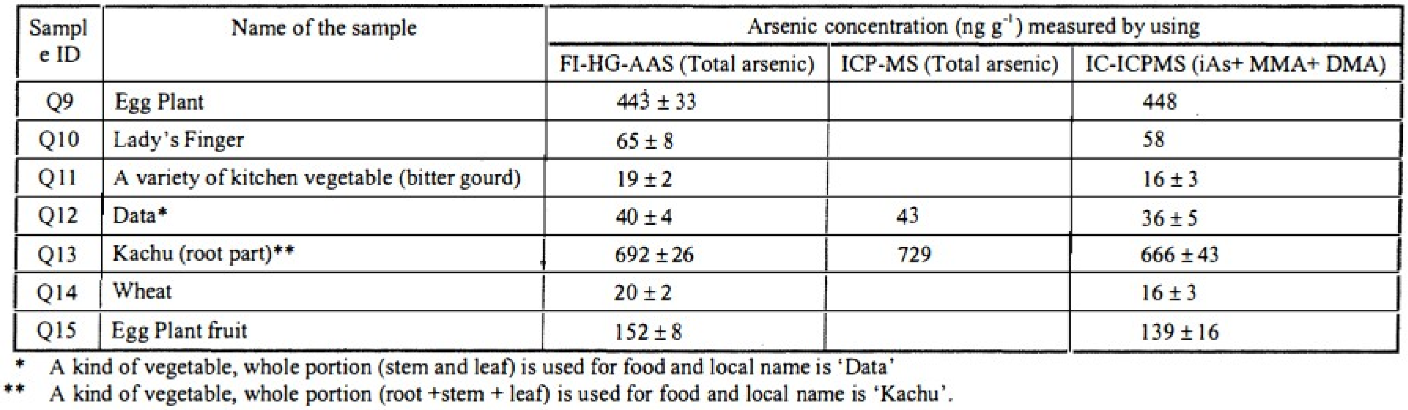
Sample ID	Arsenic concentration (ng g^{-1}) measured by using	
	FI-HG-AAS (Total arsenic) Rice	IC-ICPMS (iAs+ MMA+ DMA) Paddy (rice + husk)
Q1	120 ± 15	98 ± 2
Q2	154 ± 18	125 ± 6
Q3	137 ± 13	122 ± 6

Table 27: Arsenic concentration in same rice and paddy (rice+ husk) samples (contaminated) measured by using FI-HG-AAS and IC-ICP-MS in different laboratories.



Sample ID	Arsenic concentration (ng g^{-1}) measured by using	
	FI-HG-AAS (Total arsenic) Rice	IC-ICPMS (iAs+ MMA+ DMA) Paddy (rice + husk)
Q4	516	497 ± 22
Q5	300	270 ± 5
Q6	663	513 ± 7
Q7	633	529 ± 9
Q8	340	208 ± 11

Table 28: Arsenic concentration in same vegetables samples measured by using FI-HG-AAS, ICP-MS, and IC-ICP-MS in different laboratories.



Sample ID	Name of the sample	Arsenic concentration (ng g^{-1}) measured by using		
		FI-HG-AAS (Total arsenic)	ICP-MS (Total arsenic)	IC-ICPMS (iAs+ MMA+ DMA)
Q9	Egg Plant	443 ± 33		448
Q10	Lady's Finger	65 ± 8		58
Q11	A variety of kitchen vegetable (bitter gourd)	19 ± 2		16 ± 3
Q12	Data*	40 ± 4	43	36 ± 5
Q13	Kachu (root part)**	692 ± 26	729	666 ± 43
Q14	Wheat	20 ± 2		16 ± 3
Q15	Egg Plant fruit	152 ± 8		139 ± 16

* A kind of vegetable, whole portion (stem and leaf) is used for food and local name is 'Data'

** A kind of vegetable, whole portion (root +stem + leaf) is used for food and local name is 'Kachu'.

Total arsenic and other metal and metalloid in soil, vegetable, and paddy in some samples of West Bengal-India and Bangladesh

Along with arsenic in soil samples (n = 9), Mn, Cu, Hg, Pb, Ni & Zn were analyzed by ICP-MS after microwave digestion (Table 17). Our analysis of NIST soil sample (Table 20) by the same procedure is in well agreement. The regression analysis was carried out between arsenic and other metals. However, no significant positive or negative co-relation was observed between As & Mn (r=0.382, p=0.309), As & Cu (r=0.632, p=0.067), As & Ni (r = 0.460, p= 0.212), and As &Pb (r = 0.493, p = 0.177). A significant (<0.05) positive correlation found between As & Zn (r = 0.763, p = 0.027) and also a strong negative correlation was observed between As & Hg (r = -0.802, p = 0.009).

Table 18 shows analysis of As along with Se, Mn, Cu, Hg, Pb& Ni in rice & husk of 3 paddy samples cultivated with arsenic contaminated water. The regression analysis was carried out between arsenic and other metals. Linear regression shown negative correlation between As & Se (r= -0.999, p = 0.018), As & Pb (r = -0.992, p = 0.078) and positive correlation between As & Cu (r = 0.998, p = 0.03). But no satisfactory correction observed between As & Mn (r = -0.980, p =0.126), As & Hg (r = -0.452, p 0.70) and As & Ni (r = -0.233, p = 0.849). It has been observed selenium concentration decreases with increase arsenic concentration in both rice and husk (Table 18 & Figure 6). This has also been observed in two vegetable samples those we had studied (Table 19). All analyzed elements concentration (µg/gm) were less in "Kachu" comparing "Data" except arsenic. Arsenic was very high in "Kachu" comparing "Data" even though they were irrigated with same water containing arsenic 205 µg/L.

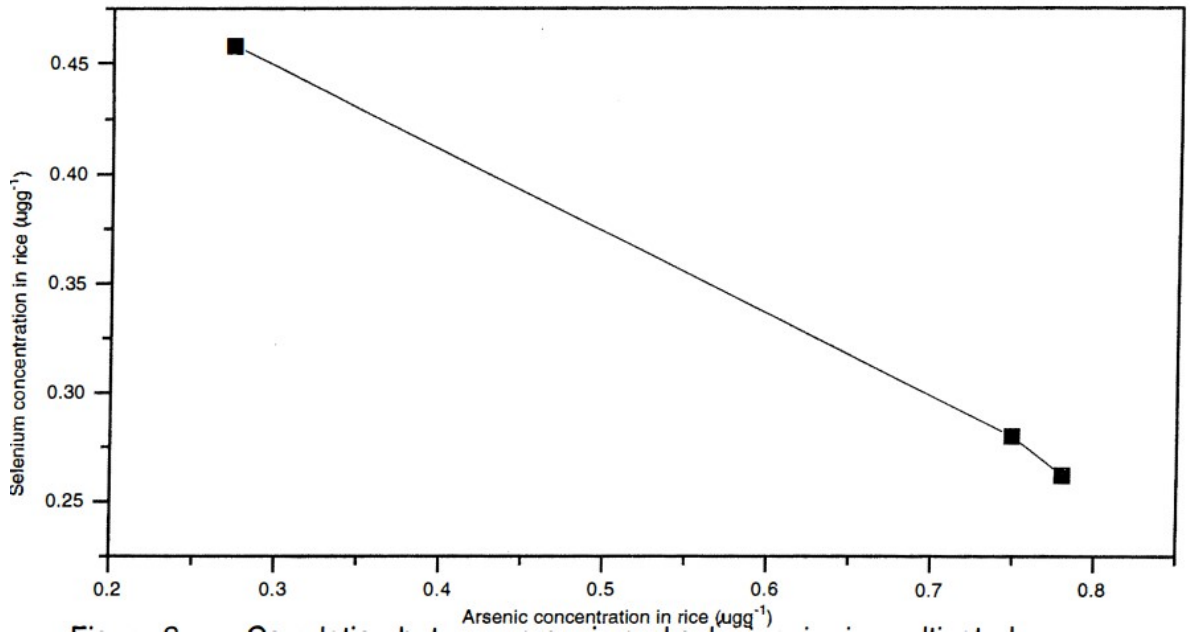


Figure 6: Co-relation between arsenic and selenium in rice cultivated by using arsenic contaminated water.

Arsenic species in vegetable, rice, and paddy in some samples of West Bengal-India and Bangladesh

Table 21 & 22 show total arsenic in groundwater used for irrigation and arsenic in soil. The sum of arsenic species in vegetable, paddy (rice + husk), rice, husk, and arsenic species in those samples from West Bengal-India & Bangladesh also shown in these table respectively. In Table As(III) and As(V) presented together as inorganic arsenic. The reason show portion of As(V) is reduced to As(III) during extraction.

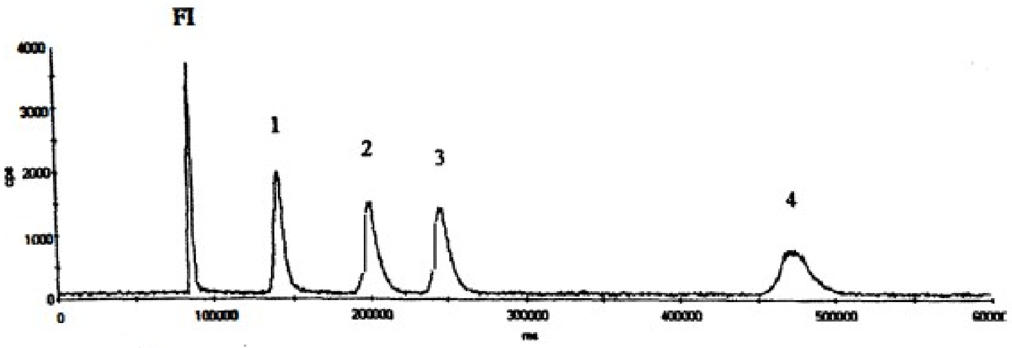


Figure 7:

: Standard chromatogram, 2 ng/mL As each peak-separation conditions: column, PRP X100; mobile phase, 10 mM $NH_4H_2PO_4$, 10 mM NH_4NO_3, pH 6.3; flow rate, 1 ml/min, sample volume, 20 μl. Detector: ICP-MS, m/z 75, 0.5 Hz sampling rate
: Peak identities: FI, 2 ng/mL As flow injection (25 μl); 1, As(III), 2, DMA; 3, MMA, 4, As(V)

Figure 7 shows the chromatogram of As(III), MMA, DMA and As(V) measured by IC-ICP- MS.

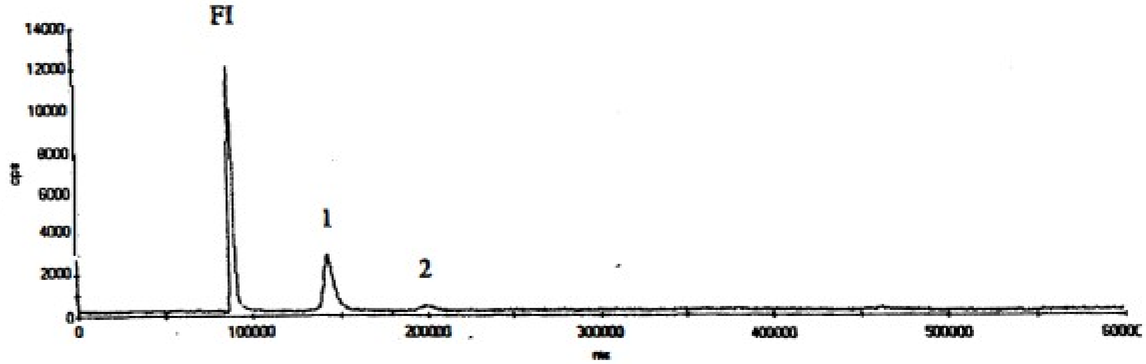


Figure 8 shows arsenic species in rice (Sample no. 1 in Table 21). It appears from all four-rice analysis that inorganic arsenic is the major portion of arsenic in rice.

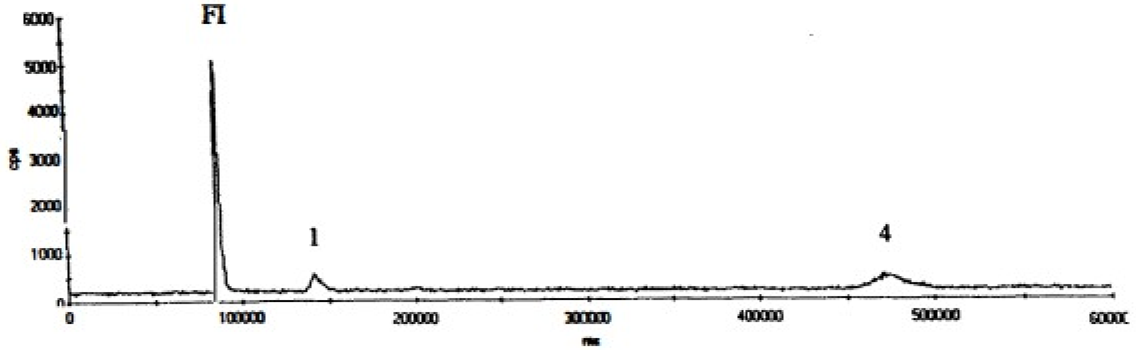


Figure 9 shows arsenic species in husk (Sample no.6 in Table 21). All four-husk analysis shows only presence of inorganic arsenic. No methylated form of arsenic was found in any husk samples.

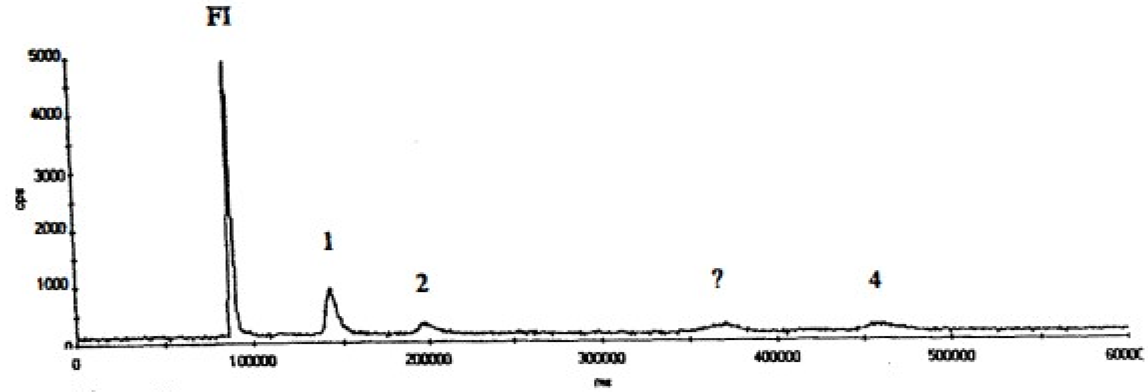


Figure 10 shows arsenic species present in lady's finger/okra (Sample no.18 in Table 21). It shows presence of inorganic arsenic & DMA, and possibility of an unknown arsenic species.

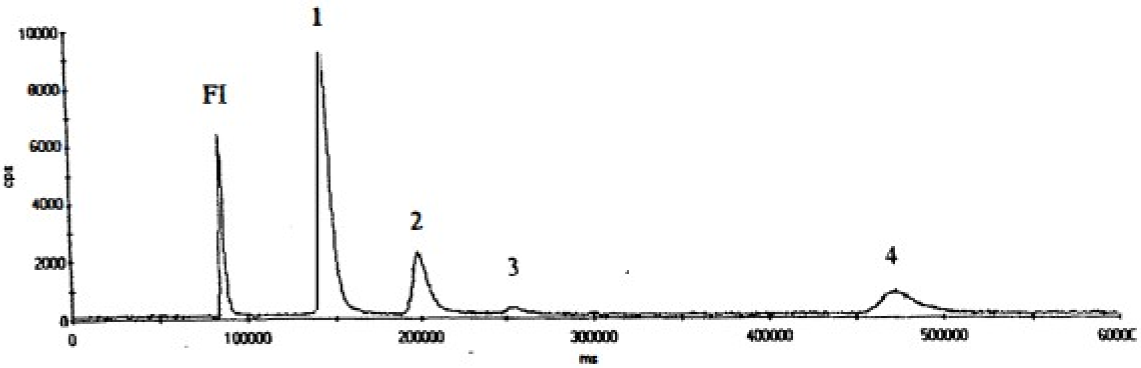


Figure 11 shows arsenic species in a paddy (rice+ husk) sample (Sample no.11 in Table 21). It has high inorganic arsenic (76.46%) and 19.37% DMA & 4.23% MMA.

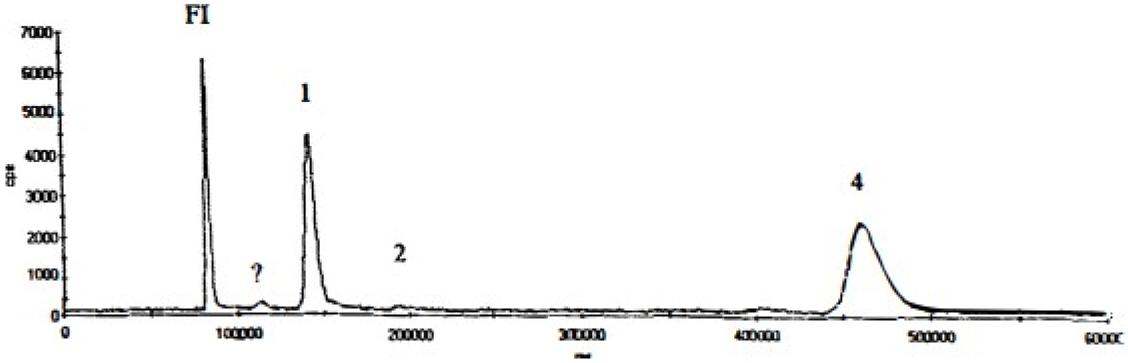


Figure 12: Sample No. 5B in Table 22; Peak identities: 1, As(III); 2, DMA; 4, As(V) and an unknown peak

Figure 12 shows very high arsenic concentration in a vegetable named "kachu" (Sample no. 5B in Table 22) which grows inside soil a popular food in West Bengal-India & Bangladesh. Most interesting, its arsenic concentration in very quite high but it has no detectable amount of methylated form of arsenic and possible of an unknown arsenic species.

The overall conclusion from arsenic analysis in rice, paddy (rice + husk) and some vegetables are that inorganic arsenic is the dominating species of arsenic.

Conclusion

Food habit and arsenic intake from food and water to those living in arsenic contaminated villages.

Rice and vegetable are the staple food for poor villagers of West Bengal-India and Bangladesh. This is true for the villagers in Kolsur gram-panchayet (G.P.) in Deganga block of North 24-Parganas district, West Bengal-India, where we studied for 21 months arsenic in soil, rice, and vegetable from 10 plots cultivated with arsenic contaminated water. Normally, 3 times villagers eat rice with mainly vegetable per day. Adults (male or female) normally eat 250 gm of rice every time i.e., 750 gm of rice per day and child (around 10 years) eat 400 gm of rice during whole day. Adults eat in average 165 gm of cooked vegetable to each meal and child around 100 gm. Average water intake per day for adult male, adult female, and child are 4 liters, 3 liters, and 2 liters, respectively. Those who work in field consume more water (average 6.0 liters) and during summer the average water intake to those work in field may go as high as 10 liters. Villagers are also consuming arsenic from Pantavat# and water added for food preparation like rice, soup, curry, and drinks like tea, lemon water, etc. After thorough discussion with the villagers, it appears that this is equivalent to consumption of 1 liter of water for adult and 500 ml for child.

Normal daily average food intake for adult to each meal is as follows:

Meal (adult)	**Type of Food**
Morning/ Breakfast	PANTAVAT# with vegetable (rice, 250 gm and cooked vegetable, 100 gm)
Lunch	Normally, rice (250) gm and cooked vegetable, 200 gm
At night	Rice (250) gm and cooked vegetable, 200 gm Villagers occasionally eat fish, egg, and rarely meat.

#PANTAVAT: This is common food for villagers of W. Bengal-India and Bangladesh at breakfast. Pantavat is rice mixed with water. Normally they pour water to the rice cooked on the previous night and have it as their breakfast. Normally, villagers eat Pantavat with vegetable/ smashed Potato/ Chili and Onion.

Total arsenic burden to the villagers from water and food

We have classified arsenic intake in three categories:

Category I Arsenic alone from contaminated drinking water.

Category II Arsenic from food (rice and vegetable).

Category III Arsenic from contaminated water added to 'Pantavat' and for food preparation (rice, soup, curry, drinks like tea, lemon water).

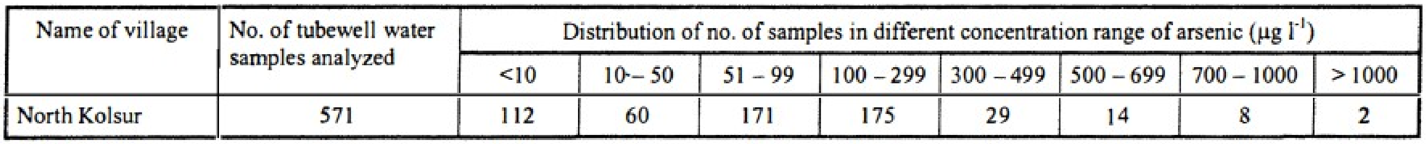
Altogether, we had analyzed 571 hand tube wells from North Kolsur village and out of these 80% tube wells contains arsenic above 10 µg/L and 70% tube wells contain above 50 µg/L. The average arsenic concentration in contaminated hand tube wells (n=399) is 200 µg/L. When we started our work in this village, villagers were drinking arsenic contaminated water. We informed them about contamination of their hand tube-wells and identified safe tube wells for them in their village. We do not know what percentage of villagers consuming safe water are, but we know for irrigation purpose they are still using contaminated tube well water. Arsenic concentration in hand tube well they were drinking is given in Table 29.

We had collected and analyzed soil, rice, vegetable, and water used for irrigation for our 10 studied fields in North Kolsur village. Arsenic concentration in 10 fields shown in Tables 3 & 10. Villagers close to our studied areas are consuming rice and vegetable from these 10 fields. Average arsenic concentration in soil (n=68), rice (n=8) and vegetable (n=30) are 22.30 µg/gm (range 7.91µg/gm to 43.08 µg/gm, dry weight), 0.358 µg/gm (range 0.120 µg/gm to 0.663 µg/gm, dry weight) & 0.034 µg/gm (range 0.008 µg/gm to 0.120 µg/gm, wet/weight), respectively. Our preliminary study indicates that edible portion that vegetable grow inside soil contain high amount of arsenic. Villagers were also using the contaminated hand tube well's water for PANTAVAT (average 200 µg As/L). Control soil (n=6), rice (n=3), and vegetable (n=3) samples contain arsenic (average) 5.84 µg/gm (range 5.31 to 6.60 µg/gm), 0.089 µg/gm (range 0.083 to 0.959 µg/gm), and 0.009 µg/gm (range 0.007 to 0.012 µg/gm), respectively.

Our preliminary study indicates, we have arsenic concentration in irrigated water of control area is <3 µg/L. Our control area was Medinipur district, which is not arsenic contaminated. It appears that the average arsenic concentration in contaminated soil, rice, and vegetable are 3.81, 3.62, and 5.66 times higher than the control samples, respectively.

Table 30 to Table 32 show arsenic burden to each villager from contaminated tube well water alone, from rice, vegetable, and from water added for Pantavat and food preparation, respectively.

Table 29: Distribution of arsenic in hand tube well water samples of North Kolsur village in Deganga block of North 24-Parganas district, West Bengal-India



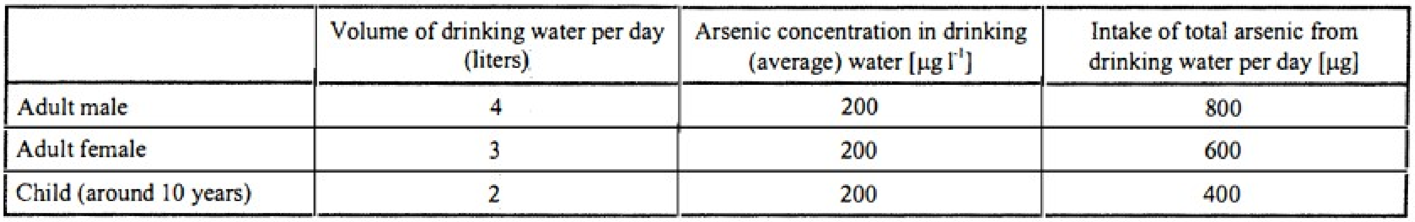
Name of village	No. of tubewell water samples analyzed	Distribution of no. of samples in different concentration range of arsenic ($\mu g\ l^{-1}$)							
		<10	10 – 50	51 – 99	100 – 299	300 – 499	500 – 699	700 – 1000	> 1000
North Kolsur	571	112	60	171	175	29	14	8	2

North Kolsur villagers body burden of total arsenic, inorganic arsenic, and organic arsenic from water, food, and water added for food preparation

Our earlier study[9] shows that arsenic compounds present in hand tube well from our study area are arsenite and arsenate. Our present rice and vegetable analysis show [preliminary study on total inorganic and organic arsenic compounds in some rice and vegetable samples measured by using IC-ICP-

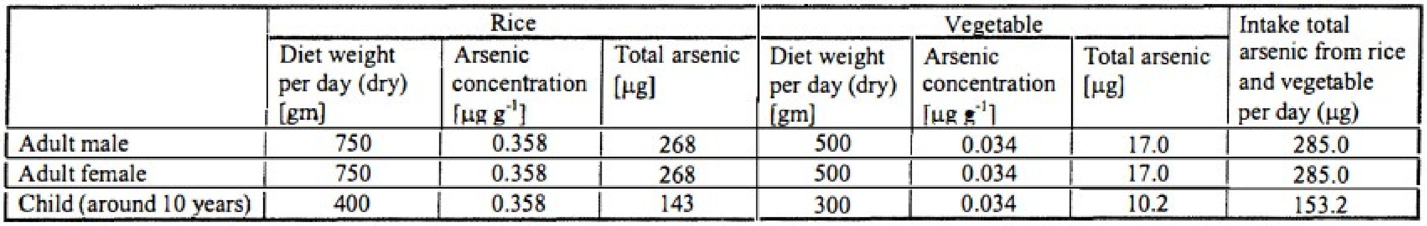
MS[10] from US Food and Drug Administration, Forensic Chemistry Centre, Cincinnati, USA] 95% and 5% are inorganic arsenic and organic arsenic in rice, and 96% and 4% of inorganic arsenic and organic arsenic in vegetable.

Table 30: Arsenic burden to each adult male, adult female, and child from water alone at North Kolsur village of Deganga block of North 24-Parganas, West Bengal-India



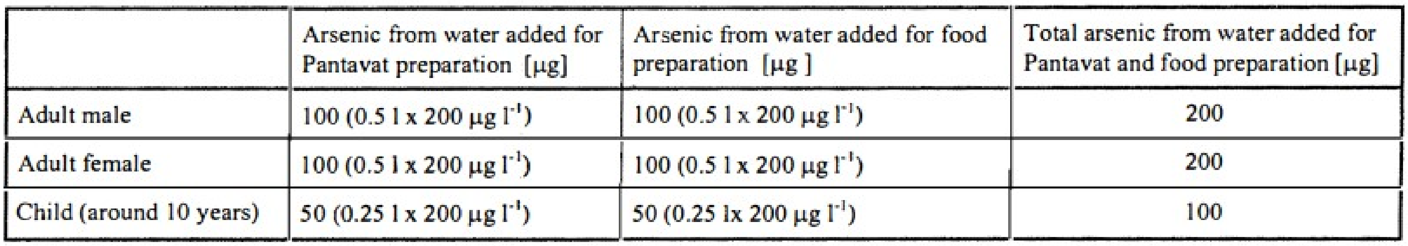
	Volume of drinking water per day (liters)	Arsenic concentration in drinking (average) water [μg l^{-1}]	Intake of total arsenic from drinking water per day [μg]
Adult male	4	200	800
Adult female	3	200	600
Child (around 10 years)	2	200	400

Table 31: Arsenic burden to each adult male, adult female, and child from contaminated rice and vegetable per day



	Rice			Vegetable			Intake total arsenic from rice and vegetable per day (μg)
	Diet weight per day (dry) [gm]	Arsenic concentration [μg g^{-1}]	Total arsenic [μg]	Diet weight per day (dry) [gm]	Arsenic concentration [μg g^{-1}]	Total arsenic [μg]	
Adult male	750	0.358	268	500	0.034	17.0	285.0
Adult female	750	0.358	268	500	0.034	17.0	285.0
Child (around 10 years)	400	0.358	143	300	0.034	10.2	153.2

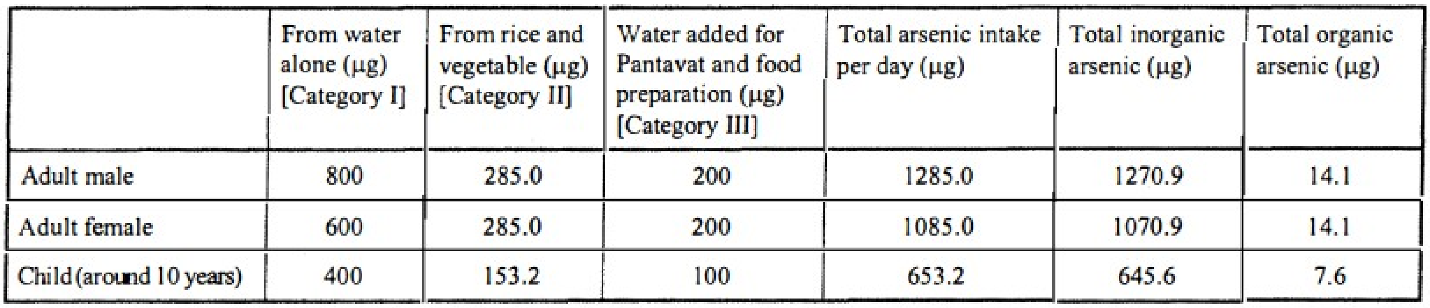
Table 32: Arsenic burden to each adult male, adult female and child from contaminated water added for pantavat and food preparation per day



	Arsenic from water added for Pantavat preparation [μg]	Arsenic from water added for food preparation [μg]	Total arsenic from water added for Pantavat and food preparation [μg]
Adult male	100 (0.5 l x 200 μg l^{-1})	100 (0.5 l x 200 μg l^{-1})	200
Adult female	100 (0.5 l x 200 μg l^{-1})	100 (0.5 l x 200 μg l^{-1})	200
Child (around 10 years)	50 (0.25 l x 200 μg l^{-1})	50 (0.25 lx 200 μg l^{-1})	100

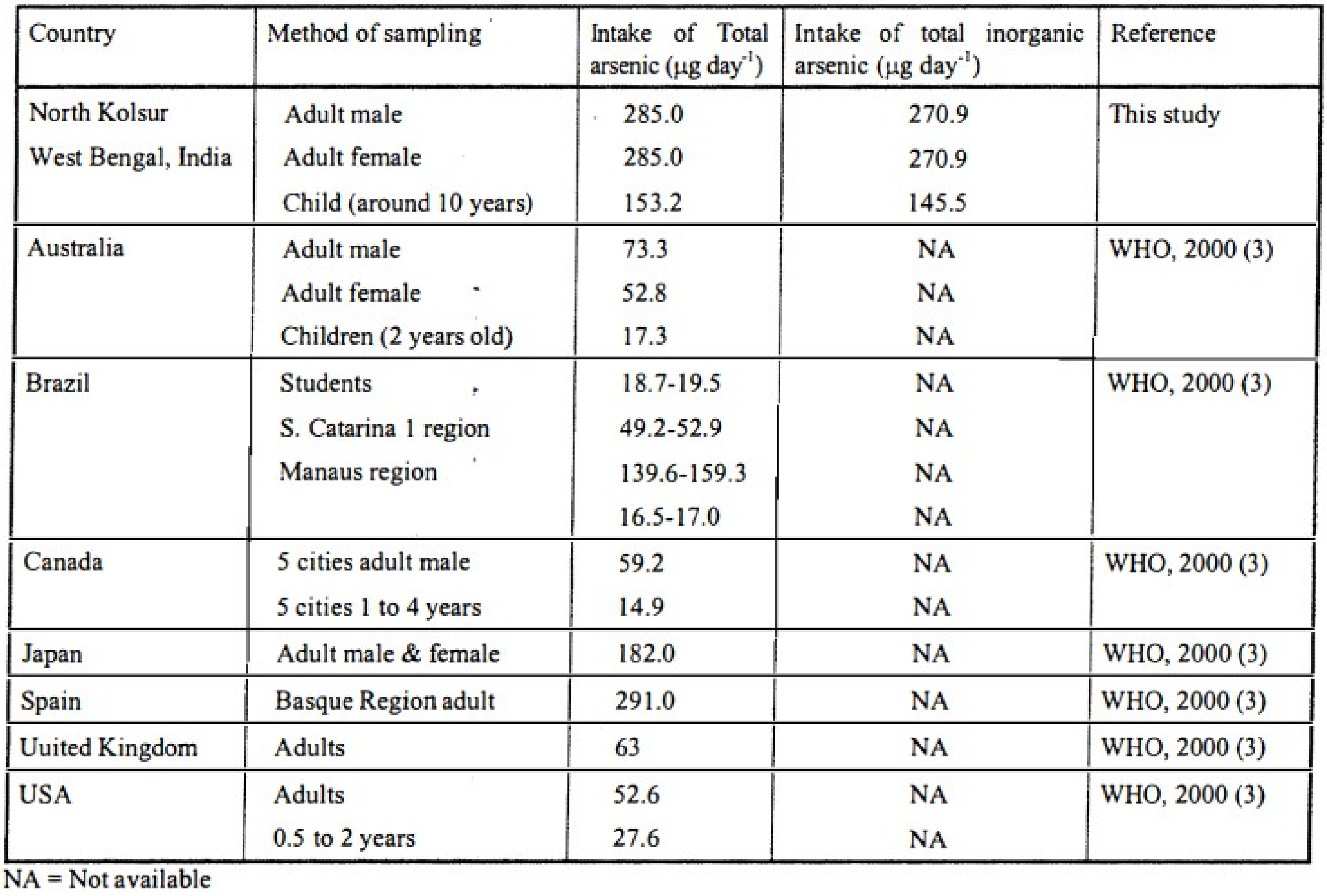
Table 33 shows arsenic burden (total, inorganic arsenic, and organic arsenic) to each adult male, adult female, and child combining category I, II and III.

Table 33: Arsenic burden to each adult male, adult female, and child combining category I, II, and III



	From water alone (μg) [Category I]	From rice and vegetable (μg) [Category II]	Water added for Pantavat and food preparation (μg) [Category III]	Total arsenic intake per day (μg)	Total inorganic arsenic (μg)	Total organic arsenic (μg)
Adult male	800	285.0	200	1285.0	1270.9	14.1
Adult female	600	285.0	200	1085.0	1070.9	14.1
Child (around 10 years)	400	153.2	100	653.2	645.6	7.6

Table 34: Arsenic from food to North Kolsur villager and from other countries



Country	Method of sampling	Intake of Total arsenic (μg day^{-1})	Intake of total inorganic arsenic (μg day^{-1})	Reference
North Kolsur West Bengal, India	Adult male	285.0	270.9	This study
	Adult female	285.0	270.9	
	Child (around 10 years)	153.2	145.5	
Australia	Adult male	73.3	NA	WHO, 2000 (3)
	Adult female	52.8	NA	
	Children (2 years old)	17.3	NA	
Brazil	Students	18.7-19.5	NA	WHO, 2000 (3)
	S. Catarina 1 region	49.2-52.9	NA	
	Manaus region	139.6-159.3	NA	
		16.5-17.0	NA	
Canada	5 cities adult male	59.2	NA	WHO, 2000 (3)
	5 cities 1 to 4 years	14.9	NA	
Japan	Adult male & female	182.0	NA	WHO, 2000 (3)
Spain	Basque Region adult	291.0	NA	WHO, 2000 (3)
Uuited Kingdom	Adults	63	NA	WHO, 2000 (3)
USA	Adults	52.6	NA	WHO, 2000 (3)
	0.5 to 2 years	27.6	NA	

NA = Not available

Table 34 shows a comparative study of inorganic arsenic and total arsenic intake of North Kolsur villagers along with some other countries[3]. The high concentration of arsenic to population in Japan, Spain, Manaus region of Brazil is due to high intake of seafood. It is also obvious that organic arsenic contributions from other countries represented in Table 34 are also substantial from seafood. North Kolsur villagers rarely consume seafood.

From the results of total arsenic (drinking water + rice + vegetable + Pantavat + water added for food preparation) body burden to North Kolsur villagers (1185.0 μg for per adult per day, 653.2 μg for per child per day), amount of arsenic coming from rice, vegetable, and water added for Pantavat and food preparation is 485 μg i.e., 41% of total for adult and 253.2 μg i.e., 38.8% for child and from rice and vegetable 285 μg i.e., 24% of total for adult and 153.2 μg i.e., 23.4% for child (around age l0 years). Our findings show most of the arsenic coming from food is inorganic in nature. As toxicity of most of the organic arsenic compounds in food is less compared to inorganic arsenic, North Kolsur people appears also at risk from arsenic in food.

According to WHO[11], 1.0 mg of inorganic arsenic per day may give rise to skin effects within a few years. It has been estimated that based upon the current U.S. Environmental Protection Agency (EPA) standard of 50 μg/L, the lifetime risk of dying from cancer of the liver, lung, kidney, or bladder, from drinking 1 liter per day of water could be as high as 13 per 1000 persons[12]. Using the same methods, the risk estimate for 500 μg/L of arsenic in drinking water would be 13 per 100 persons[13]. In its latest document on arsenic in drinking water, the U.S. National Research Council (NRC) concluded that exposure to 50 μg/1 could easily result in a combined cancer risk[14] of 1 in 100. Comparing to the WHO, EPA, and NRC document with arsenic burden to Kolsur villagers from water and food it appears that Kolsur villagers' risk of suffering from arsenical skin effect and cancer is there. Compared to worldwide arsenic consumption from food, it appears Kolsur villagers are also consuming high amount of inorganic arsenic from food and vegetable. Kolsur village is an example of many such villages in West Bengal-India and Bangladesh.

Further, products from arsenic irrigated water- soil system rich in arsenic are also coming to common marketplace far away from contaminated areas and even people who are not drinking arsenic contaminated water may get arsenic from food products produced from contaminated fields. In West Bengal-India and Bangladesh rice, vegetable, and other products are coming to cities (including Kolkata in West Bengal-India and Dhaka in Bangladesh) from villages and possibility that city people consuming arsenic contaminated products from contaminated areas cannot be ruled out.

In one of our studies[2] we mentioned that arsenic in urine (metabolites) to a group of controlled population using water for drinking and cooking having arsenic <3 μg/L, have arsenic in their urine higher than normal level. This explains that a high background level of arsenic is resulted to the surroundings of arsenic contaminated area due to arsenic coming from food chain.

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Reference

1. Mandal, B.K., Chowdhury, T.R., Samanta, G., Basu, G.K., Chowdhury, P.P., Chanda, C.R.,Lodh, D., Karan, N.K., Dhar, R.K., et al (1996). Arsenic in groundwater in seven districts ofWestBengal,India-thebiggestarseniccalamityintheworld.Current Sci.,70(2),976-986.
2. Mandal, B.K. (1998). Status of arsenic problem in two blocks out of sixty in eight groundwaterarsenic affected districts of West Bengal - India (Ph.D. Thesis). Jadavpur University, Calcutta,India.
3. WHO. Arsenic (2000).:Environmental Health Criteria. Geneva, Switzerland: World HealthOrganization. Chapter 5: p. 27.
4. Weiler, R. R. (1987) Unpublished data. Ministry of the Environment Rep. 87-48-45000-057, Toronto, Ont. Data presented in reference 5.
5. Debeka, R. W. et al (Jan Feb-1993). Survey of arsenic in total diet food composites and estimation of the dietary intake of arsenic by Canadian Adults and children. Jour. AOAC, 76:1:14.
6. USEPA. Special Report on Ingested Inorganic Arsenic. Skin Cancer; nutritional essentiality,EPN625/ 3-87/013, Washington DC (1988).
7. National Academy of Sciences (1977): Arsenic:The National Research Council (NRC), Washington DC, p332.
8. Jacobs,L.W., Keeney,D.R., and Walsh,L.M. (1970). Arsenic Residue Toxicity to Vegetable and Crops Grown on Plainfield Sand. Agronomy J., 62,588-591.
9. Chatterjee, A., Das, D., Mandal, B.K., Roy Chowdhury, T., Samanta, G., Chakraborti, D. (1995). Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part I: Arsenic species in drinking water and urine of the affected people. The Analyst, 120, 643-650.
10. Douglas, T.H., Nohora, P.V., Kirsten, R.S., Craig, S.W. (2001). Determination of total and speciated arsenic in rice by ion chromatograpyh and inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom., 16: 299-306. Perarce, F. (1998). Arsenic in water. The Guardian (UK), 19/25 February, 2-3.
11. WHO. Arsenic (1981): Environmental Health Criteria 18. Geneva, Switzerland: World Health Organization.
12. Smith, A.H. et al. (1992). Cancer risks from arsenic in drinking water. Environmental HealthPerspectives. 97: 259-267.
13. Smith, A.H. et al. (1999). Cancer risks from arsenic in drinking water: Implications for drinking water standards. In: Proceedings of the Third International Conference on Arsenic Exposure and Health Effects, 12-15 July 1998, San Diego, Elsevier Science Ltd.,Oxford, UK. pp 191-200.
14. National Research Council (1999). Arsenic in drinking water. Washington,DC, National Academy Press.