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Assessment of Arsenic content in water, soil and plant samples of Patna

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ABSTRACT

The aim of present study was to develop a database of Arsenic (As) in groundwater, soil, vegetables, cereal and forage crops to evaluate the potential human health risks posed by a higher level of As, in Maner block of Patna, Bihar. The total concentration of arsenic in various samples under study was determined by hydride generator atomic absorption spectrophotometer. The concentration of Arsenic in ground water, soil and plant samples exceeded the WHO guideline values (10 ppb). The concentration of As in groundwater (tubewell) used for irrigation and agricultural soil samples ranged between 11.07 to 91.72 ppb and 82.2-135.5 ppb, respectively, which was on an average above the permissible limit of WHO guideline value. Soil of the study area was slightly acidic to alkaline in nature with low range of nitrogen and medium range of P and K.Crops were sampled from the selected sites and result showed that in vegetables As content varied in the range of 50.8 ppb to 289.1 ppb, in forage/pulse in the range of 90.3 ppb to 241.5 ppb and in cereal (Maize)crop in the range of 40.1 ppb to 265.4 ppb. Above ground concentration of arsenic in vegetables (consumable portion) was found to be higher than cereal and forage crops.

Keywords: Arsenic, Contamination, Forage, Groundwater, Plant, Soil, Vegetables

INTRODUCTION

Arsenic is metalloid with atomic number 33 and atomic weight 74.92. The most common oxidation states of arsenic are –3 (arsenide, usually alloy like compound), +3 (arsenite, As (III), organo arsenic compound), +5 (arsenates, As (V), most stable inorganic arsenic oxi-compound). It can exist both in organic and inorganic forms. However, inorganic forms are more toxic than organic. Arsenic is found in all natural environments in abundance in earth's crust and in small quantities in rock, soil, water and air. It is introduced in soil and ground water during weathering of rocks followed by leaching and run off, it can also be introduced from anthropogenic sources due to the dumping of untreated discharge and hazardous waste materials from industries (Chatterjee and Banerjee, 1999).

In ground water inorganic arsenic is commonly present as arsenate (As V) and Arsenite (As III), inter-conversion of which takes place by oxidation-reduction (CGWB, 2013). Klump *et al.*, (2006) critically analyzed the negative impact on the flow system in the upper 30 m due to irrigation pumping. The concentration of arsenic increased proportionally to the increasing groundwater age for the upper 20 m of the aquifer in Bangladesh. There is extensive withdrawal of groundwater for domestic use and irrigation (Dikinya and Areola, 2010). A large number of water bodies around the world are reported to have arsenic (As) contamination levels at concentrations above 10 μg/l (Permissible limit of As by WHO). Arsenic concentration >10 μg/l in drinking water is casually related to increased risks of cancer in the skin, lung, bladder and kidney, as well as other skin change such as hyperkeratosis and pigmentation change, increased risks of lung and bladder cancer. The most noteworthy occurrences are located in parts of Argentina, Bangladesh, Chile, China, Hungary, India and parts of the USA, and South East Asia. The situation of as toxicity in India is alarming with reports of severe health problems among the populations of various states including West Bengal, Bihar, Assam, Chhattisgarh, etc. (Mukherjee *et al.*, 2003). The high concentration of As in groundwater has been reported from the Bengal Delta Plains (BDP) in West Bengal and Bangladesh (Dhar *et al.*, 1997). More recently, problems have also been found in the states of Arunachal Pradesh, Assam, Bihar, Nagaland, Manipur, Mizoram, Meghalaya, Tripura, and Uttar Pradesh (Mukherjee *et al.*, 2003). Way back in 1980, the Government was aware that eight districts of West Bengal and two districts of Chhattisgarh are severely affected with arsenic contamination in Groundwater. Later on, in 2002 the arsenic contamination was reported in *Semria Ojha* Patti village in Bhojpur and Patna districts of Bihar. The further investigations were carried out and it was found that Groundwater of Bhojpur, Buxar, Paschimi Champaran, Purbi Champaran, Sitamarhi, Madhubani, Supaul, Araria, KishanganjPurnea and Katihar Districts of Bihar is contaminated with Arsenic and As is above the permissible limit (Chakraborti *et al.* 2001). The results of above investigations support the earlier theory of areas near the Gangetic plains and the Padma-Meghna-Brahmaputra basin, where arsenic is present naturally due to the geological activities of rivers and have deposited arsenic sediments across these basins (CPCB, 2007). The primary source of

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Arsenic is in association with iron oxy-hydroxide in aquifer sediment and the key process of Arsenic mobilization is desorption and dissolution of iron-oxides due to the reducing conditions of the aquifer and low hydraulic gradients. But this theory does not explain the increasing Arsenic concentration in existing tube wells, previously safe but now progressively contaminated (Chakraborti *et al.,* 2001). Arsenic in soils is normally bounded to clay containing amorphous aluminum and iron oxyhydroxides. The mobility of arsenic depends on the kind of soil, pH, and on the iron, aluminum and phosphate contents. It has been observed that a drop in pH and an increase in fulvic acid increase arsenic leaching. Displacement of As by P from the sorption sites increases arsenic mobility in the soil when there is no plant root to absorb the As from the soil solution. This is consistent with the mechanism of P-enhanced release of As in the soil and subsequent promotion of As movement through the soil by the competition of dissolved As and P for ion adsorption sites. Phosphate addition significantly increased the amount of As leached from the soil (Cao *et al*., 2003). Vegetables, which grow very fast, accumulate much more As compared to cereals. Arsenic pollution in soils also has effects on vegetation and easily affects the animals that graze on grass. The amount of soil arsenic removed by a plant (uptake biomass) can be used to better determine the efficiency of a plant to concentrate arsenic from the soil into its biomass (Fayiga *et al.,* 2007), which can be used as an indicator plant in bioremediation of the heavy contaminated site.

Therefore, the present study was taken to assess the distribution and levels of Arsenic contamination in three environmental components i.e. soil, water as well as vegetation grown in the region.

MATERIALS AND METHODS

Study area

Maner is situated on the bank of Ganga, Sone and Saryu rivers and lies 24 km west of Patna the capital of Bihar on national highway 30. Whole of the area forms part of Indo-Gangetic alluvium. Patna has a humid subtropical climate with extremely hot summers from late March to early June, the monsoon season from late June to late September and chilly winter nights and foggy or sunny days from November to February with mean temperature annual of 26°C with a mean maximum of 34.6°C and mean minimum of 16.7°C. The mean annual average rainfall is 1180mm.

Sampling

Villages and *tolas* selected for the study area (after discussion with Central Groundwater Board, Patna) were Sherpur Masjid, Chihtthar (Vaishali Rai), Chihtthar (Asharfi Rai), Ratantola, Jivrakhandtola, Baba chowk and Nayatola.

Water: Water samples were collected from different water sources in vials which were pre-treated with dilute acid. Before filling, bottles were rinsed two or three times with the water being collected. After collection, the sample was acidified with concentrate nitric acid to a pH below 2 to minimize precipitation and adsorption of heavy metals on the container walls (Cornelis *et al.,* 1995). After acidifying sample were transferred to the lab and kept in a refrigerator at 4ºC temperature until further analysis.

Soil: Soil samples from the 0-15,15-30,30-45,45-60,60-75 cm soil layer were taken at 3 locations in each field adjacent to tube-well from which water was used for irrigation were collected from the field using a core sampler of 8 cm diameter. The samples were transported in dried acetone-cleaned polyethylene bags to the lab for further analysis.

Plant: Samples of different crops (roots, stem, leaves and fruit) available in the field at the time of sampling surrounding the tube-wells from which the water samples were collected for further analysis.

Sample Preparation

Water: The water samples were filtered through Whatman no-42 filter paper to obtain clear samples; these were properly labeled and stored for further analysis.

Soil: The soil samples were air-dried and then ground to pass through a 2 mm sieve. These samples were stored into properly marked polythene packets, appropriately sealed, and stored for measurement of their arsenic contents. Then 1g of the given soil samples were taken in digestion tube and digested on a sand bath (100°C) with tri-acid mixture (HNO_3: H_2SO_4: $HClO_4$: 10: 1: 4, by volume) to obtain clear digest, At the same time soil samples were analyzed for other physicochemical properties.

Plant: In the laboratory, plant samples were rinsed with tap water and scrubbed with a laboratory nylon brush until all soil was removed after they were rinsed several times with distilled water and finally with deionized water. Then plant samples were processed so as to obtain various parts like root, shoot, leaf and economic produce or the whole samples as demanded by the nature of the plant and weed sample collected. Such separated plant portions were appropriately labeled, dried in hot air-oven at 60°C for 72 hours. The dried plant samples were grounded to powder. Then 0.5g of the given soil samples were taken in digestion tube and digested on a sand bath (100°C) with tri-acid mixture (HNO_3: H_2SO_4: $HClO_4$: 10: 1: 4, by volume) to obtain clear digest.

Analysis

A Perkin-Elmer Model 460 atomic absorption spectrophotometer equipped with an MHS-10 Mercury/Hydride System was used. A Perkin-Elmer arsenic electrode less discharge lamp was used as a light source. Measurements were made with deuterium background correction. The samples were digested with tri-acid mixture (HNO3: H2SO4: HClO4: 10:1:4, v/v)until a clear solution was obtained. These digested materials were adequately filtered through Whatman No. 42 filter paper. The filtrate (10 ml) was taken in 50 ml volumetric flask and 5 ml conc. HCl and 1 ml mixed reagent [5% KI (w/v) + 5% ascorbic acid (w/v)] added to it. The flasks were kept as such for 45min. to ensure complete reaction and volume was made up to 50 ml. The total As content in solution was determined by using atomic absorption spectrophotometer (AAS), Perkin Elmer Analyst 200 coupled with Flow Injection Analysis System (FIAS 400) where the carrier solution was 10% HCl (v/v) following the Olsen method. A set of standard solutions of 2.5, 5.0, 10.0, and 20.0 mg L^{-1} As were used for calibration.

RESULTS AND DISCUSSION

High concentrations of Arsenic in water, soil and plant have been associated with natural processes. Due to the toxicity of As to plants, animals and human, it is desirable to understand its behavior in the environment, proposed, on the basis of sediment analysis, that oxygen entering the aquifer due to heavy groundwater withdrawal for irrigation favors the oxidation of arsenic-rich iron sulfide and mobilization of arsenic to the aquifer which was the actual cause of As contamination in Bihar.

Arsenic content in water samples

Arsenic concentration in water samples ranged from 11.07 ppb to 91.72 ppb with an average value of 53.65 ppb in all the selected area in Maner, Patna. The highest value was found in Nayatola while the lowest value was at Sherpur Masjid (Table 1). Earlier maximum permissible limit of arsenic for drinking water was 50 ppb. But now the World Health Organization (WHO) has reduced its permissible limit to 10ppb for drinking water purpose. In India, Department of Drinking Water Supply Ministry of Rural Development has still kept a limit of 50 ppb.

Table 1: Arsenic content in groundwater (Tube well) samples collected from farms located in different region of Maner block, Patna

Location	Code	Latitude	Longitude	As concentration (ppb)	Above/below permissible limit (50ppb)
Sherpur Masjid	A	25°35.633'	85°04.894'	11.07	Below
Chihtthar (Vaishali Rai)	B	25°39.489'	84°53.357'	42.06	Below
Chihtthar (Asharfi Rai)	C	25°26.463'	84°53.675'	56.2	Above
Ratantola	D	25°35.633'	84°55.335'	69.95	Above
Jivrakhandtola	E	25°38.627'	84°55.910'	14.36	Below
Baba chowk	F	25°41.209'	84°52.342'	90.21	Above
Nayatola	G	25°40.387'	84°52.278'	91.72	Above

Arsenic content in soil samples:

Arsenic content in soil samples was found above the permissible limit at all the selected places of sampling and it ranged from 82.2-135.5 ppb with the highest value in Chihtthar (Vaishali Rai) and lowest in Sherpur Masjid (Fig. 1).

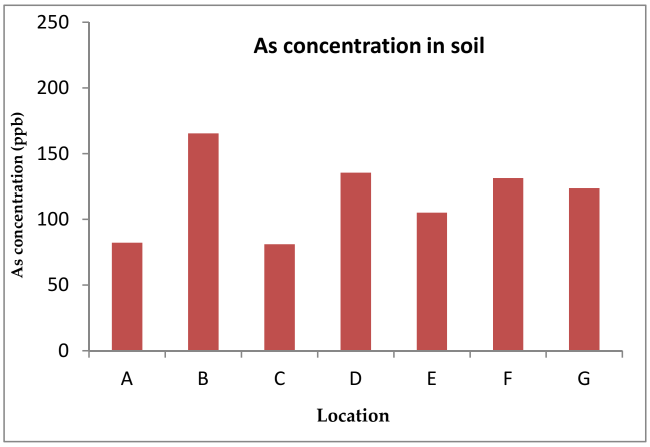

Fig.1: As concentration in soil samples from farms of Maner block, Patna

Soil profile study revealed that the Arsenic content was increasing with depth as it was lowest in 0-15 cm soil depth and was increasing in the depth range of 15-75 cm. In 0-15 cm soil depth the value of As was found as 73.9 ppb whereas in 60-75 cm soil depth value of As was167.5 ppb (Fig. 2).

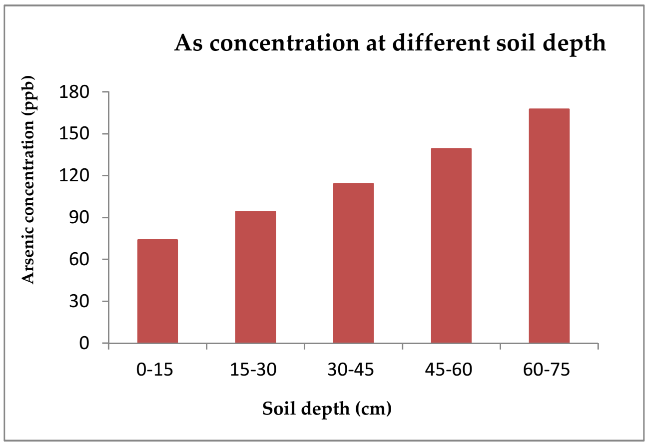

Fig. 2: Variation in Arsenic content with soil depth

Physicochemical properties of soil samples

The physicochemical properties of soil samples collected from selected locations at different soil depths are presented in Table 2. The pH of the soil samples at all the selected sites varied in the range of 6.5-8.2 in soil depth of 0-75cm, which showed that the soil of Maner block, Patna is slightly acidic to alkaline in nature. Similarly, EC (dS/m) was also found to be similar at all the selected sites with a value of 0.02-0.07 dS/m. However, within the soil profile, it was having a higher value at 0-15cm soil depth with an average value of 0.05dS/m whereas for 15-75cm depth it was found as 0.02 dS/m.

Available N content in the soil ranged from 125.4-257.2 kg/ha with the highest value in Jivrakhand tola and lowest value in Baba Chowk, respectively. While studying the soil profile, 0-15 cm soil depth had the highest value of 257.2 kg/ha and 60-75cm soil depth had the lowest value of 144.3 kg/ha. It may also be observed that at all the seven places in Maner block and in soil profile between 0-75 cm available N is in low range i.e. <281kg/ha. Available P was found in the range of 6-26.7kg/ha with the highest value in Jivrakhand tola and lowest in Sherpur Masjid. The P content was marginally higher in 0-15 cm soil depth atJivrakhand tola as compared to recommend one, otherwise, it was also lower than the desired limit. When going down the soil profile highest value was in 0-15cm as compared to 15-75 cm depth.

Similarly available K content in the soil ranged from 178.2-307.4kg/ha with the highest value in Baba chowk and lowest value in Chihtthar (Vaishali Rai), respectively. The available K content was found the maximum in 0-15 cm soil depth as compared to soil depths 15-75 cm at all the locations except at Chihtthar (Vaishali Rai). Data reveals that at all the seven locations in Maner block, Patna, available K in the soil is in the medium range.

Table 2: Physicochemical properties of soil collected from farms located in the different region of Maner block, Patna

Parameters	**Soil depth (cm)**	**Location code**						
		A	**B**	**C**	**D**	**E**	**F**	**G**
pH	0-15	7.6	8.1	7.9	7.6	6.5	8.0	7.9
	15-30	7.8	7.8	7.8	7.7	7.5	8.0	8.1
	30-45	7.8	7.8	7.8	7.6	7.5	8.0	8.0
	45-60	7.8	7.7	7.6	7.6	7.6	7.9	8.0
	60-75	7.9	7.8	7.6	7.7	7.7	7.9	8.2
EC(dS/m)	0-15	0.03	0.06	0.04	0.03	0.06	0.07	0.04
	15-30	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	30-45	0.02	0.02	0.02	0.03	0.02	0.02	0.02
	45-60	0.02	0.02	0.03	0.03	0.02	0.02	0.02
	60-75	0.02	0.02	0.02	0.02	0.02	0.02	0.02
N(kg/ha)	0-15	231.3	207.0	238.3	247.7	257.2	207.0	200.8
	15-30	250.9	232.1	225.8	185.0	175.6	125.4	200.7
	30-45	181.9	200.7	119.2	207.0	181.9	219.5	219.5
	45-60	138.0	225.8	181.9	197.6	181.9	194.4	194.4
	60-75	225.8	144.3	156.1	185.0	175.6	219.5	200.7
P(kg/ha)	0-15	12.8	13.3	13.6	15.7	26.7	24.2	23.4
	15-30	6.0	7.4	10.4	11.0	21.0	16.0	19.6
	30-45	7.0	10.9	8.4	8.6	18.6	17.6	21.4
	45-60	7.7	8.4	7.8	8.0	14.3	16.2	18.9
	60-75	6.7	11.1	7.8	11.1	10.3	16.4	17.9
K(kg/ha)	0-15	208.4	178.2	277.9	233.5	282.8	307.4	294.5
	15-30	211.6	203.8	233.9	221.0	255.5	227.0	267.3
	30-45	211.9	201.7	220.6	225.1	231.1	235.7	269.6
	45-60	186.1	224.0	203.8	219.9	227.4	242.4	257.4
	60-75	222.5	193.8	213.3	205.7	217.5	237.4	282.4

Arsenic concentration in plant samples

It was observed that As was accumulating in different crops grown in the study area due to irrigation with As-contaminated water (Table 3). Arsenic content was analyzed in different plant parts i.e. root(below ground part), leaf stem and fruit (above ground part) in various crops grown in the area at the time of sampling depending on the availability.

Arsenic content in cereal *i.e.* maize in this case, was analyzed at different locations wherever available and was found in the range of 40.1 ppb (leaf) in Nayatola to 265.4 ppb (root) in Ratantola, while in case of Forage crop (in this case *Faba bean)* As content was found to be lowest at the concentration of 90.3ppb (root) in Chihtthar (Vaishali Rai) and highest in Chihtthar (Asharfi Rai) with a value of 241.5 ppb (stem).

When different vegetables, available at that time, were compared at different locations, it was found that the lowest

Arsenic content was in tomato stem at Nayatola with a value of 50.8 ppb while the highest value was found in brinjal fruit i.e. 289.1 ppb in Chihtthar (Asharfi Rai)region (Table 3).

Table 3: Arsenic content of plant samples collected from farms located in the different region of Maner block, Patna.

Location	Crop	Root	Stem	Leaf	Fruit
		Cereal			
B	Maize (tillering)	121.3	163.8	125.3	NA
C	Maize (Fruiting)	NA	NA	NA	41.1
D	Maize (tillering)	241.5	231.1	58.25	NA
D	Maize (Fruiting)	NA	NA	211.3	NA
E	Maize (tillering)	134.2	91.6	40.1	NA
		Forage/Pulse			
B	Faba bean(tillering)	90.3	170.7	NA	NA
C	Faba bean (tillering)	124.3	265.4	NA	NA
C	Faba bean (Fruiting)	135.3	191.3	167.3	NA
F	Grass	112.4	158.6	NA	NA
		Vegetables			
C	Brinjal	134.4	102.9	187.9	289.1
C	Lady's-finger	NA	201.4	133.2	278.4
C	Sponge guard	133.6	148.8	141.4	208.9
D	Tomato	NA	90.4	121.5	NA
E	Sponge guard	NA	215.6	194.3	279.6
F	Bottle-Guard	90.5	134.7	254.3	51.3
F	Cowpea	NA	186.4	287.6	29.8
F	Tomato	NA	156.3	251.7	211.6
F	Cowpea	94.2	210.3	193.5	NA
F	Lady's Finger	NA	212.4	225.7	212.3
F	Bottle-guard	NA	158.5	190.3	234.3
F	Brinjal	NA	133.8	148.9	201.5
G	Lady's Finger	NA	NA	135.7	187.6
G	Tomato	NA	50.8	145.7	176.8
G	Ash-Guard	NA	115.7	NA	190.9
G	Cowpea	NA	NA	201.6	202.1

When overall above and below ground parts were compared it was found that Arsenic content was more in above ground parts in vegetables and forage crop compared to cereals (Fig. 3).

CONCLUSION

The present study revealed that As in irrigation water can result in soil pollution as well as food chain contamination. The continuous contamination of soil is a growing threat to crop production itself and thus to sustainable agriculture because As in soils will become toxic to plants and other organisms at a certain level. With the continuation of uncontrolled use of contaminated water in long run in

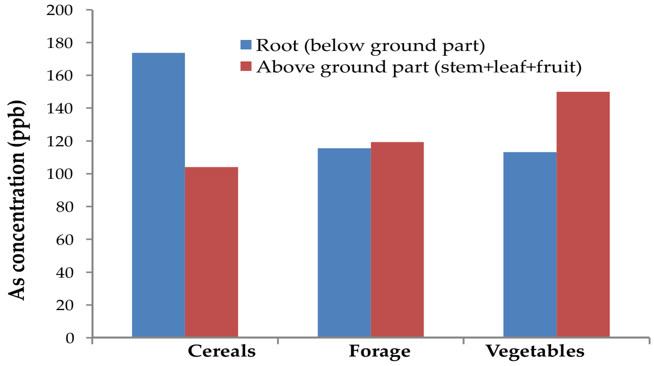

Fig. 3: Distribution of Arsenic content in different crops

agriculture, it is expected that the risks will increase over time. In the long run, it may offset ongoing efforts in the drinking water sector to reduce the adverse impacts of As.

Therefore a long-term study on the interaction between water-soil-plant-atmosphere should be done taking into account differences in soil, climatic, hydrological, biological, economic and cultural conditions between countries and within them.

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