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Arsenic contamination in ground water: an environmental issue

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1. Introduction

Arsenic (As) is a naturally occurring element in the earth's crust and is found throughout the environment. Increased As concentration in groundwater is generally associated with geogenic sources (Nordstrom, 2002; Smedly and Kinniburgh, 2002; Chakraborti *et al.* 2010; Sanyal, 2013) and has positive interaction with soil minerals (Kima *et al.* 2012). Of late, groundwater contamination in the Bengal delta basin of the Indian sub-tropics and Bangladesh, bound by the rivers Ganga and Padma, is of great concern to the world since the latter affects the soil-plant-animal/ human systems.

2. Arsenic toxicity in soil-plant-animal-human system

Arsenic (As), a toxic trace element, is of great environmental concern due to its presence in soil, water, plant, animal and human continuum (Sanyal, 1999; Sanyal and Nasar, 2002). Its high toxicity and increased appearance in the biosphere has triggered public and political concern. Out of 20 countries (covering Argentina, Chile, Finland, Hungary, Mexico, Nepal, Taiwan, Bangladesh, India and others) in different parts of the world where groundwater arsenic contamination and human suffering therefrom have been reported so far, the magnitude is considered

Table 1: Groundwater arsenic contamination in the Indian subcontinent

State	Coverage	Level of contamination	Citation
West Bengal	**12 districts** (Mushidabad, Maldah, Nadia, North 24 Parganas, South 24 Parganas, Bardhaman, Howrah, Hooghly, Kolkata, Coochbehar, North Dinajpur and South Dinajpur), **111 blocks**	50-3700 µg/l	http://www.soesju.org /arsenic/wb.htm
Assam	**18 districts, 72 blocks** **5 districts** (Barpeta, Dhemaji, Dhubari, Darrang and Golaghat) **4 districts** (Jorhat, Lakhimpur, Nalbari and Nagoan)	>50 µg/l 100 - 200 µg /l 228–657 µg /l	Singh, A. K. (2007) Curr. Sci. **92** (11): 1506-15
Bihar	**12 districts (**Bhagalpur, Khagaria, Munger, Begusarai, Lakhisarai, amastipur, Patna, Baishali, Saran, Bhojpur, Buxar, and Katihar)**, 32 blocks and 201 villages.**	> 50 µg/l	Acharya, S.K. and Shah, B.A. (2004) *Env. Health Perspective* **112** (1); 19- 20
Jharkhand	**1 district** (Sahibgunj)	> 50 µg/l	http://www.soesju.org /arsenic/jharkhand.htm
Uttar Pradesh	**21 districts** (Ballia, Lakhimpur, Kheri, Bahraich, Chandauli, Ghazipur, Gorakhpur, Basti, Siddarthnagar, Balrampur, Sant Kabir Nagar, Unnao, Bareilly, Moradabad, Rae Bareli, Mirzapur, Bijnore, Meerut, Sant Ravidas Nagar, Shahjahanpur and Gonda)	> 50 µg/l	http://www.nerve.in/ news:253500133730
Madhya Pradesh	**1 district** (Rajnandgaon)	52-88 µg/l	*Press Trust of India, September 4, 1999*
Manipur	**1 district** (Thoubal)	798-986 µg /l	Singh, A. K. (2007) Curr. Sci. **92** (11): 1506-15
Tripura	**3 districts** (North Tripura, Dhalai and West Tripura)	65-444 µg/l	
Nagaland	**2 districts** (Mokokchung and Mon)	> 50 µg/l	

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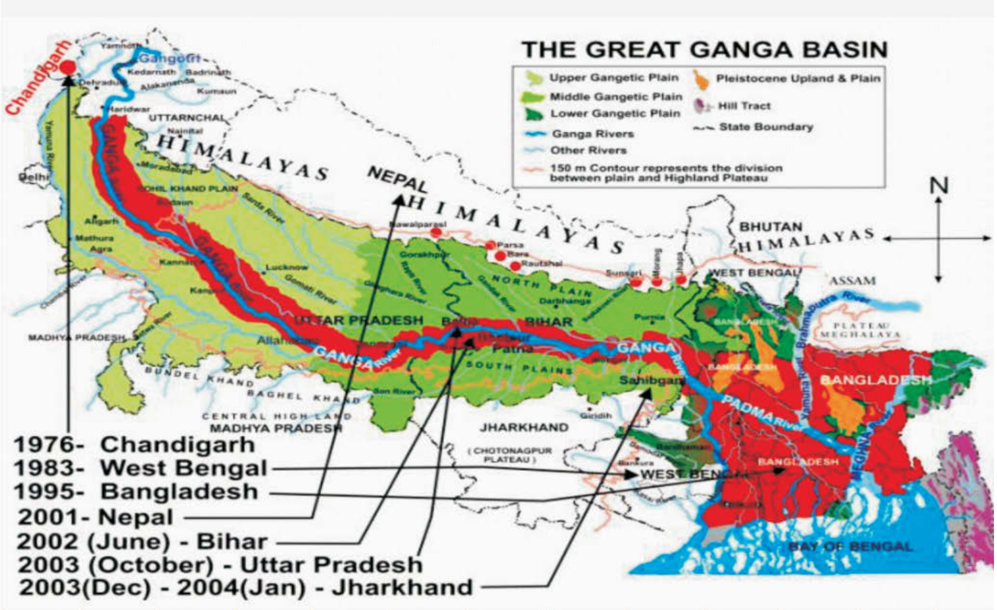

Fig. 1 : Groundwater arsenic contamination in the Indian Subcontinent **Source :** *Sanyal (2005)*

Photograph By: Santanu Saha

Village: Nonaghata-Uttarpara Block: Haringhata Dist.: Nadia, West Bengal

Photograph By: Santanu Saha

Villege: Ambikanagar Block: Deganga Dist.: North-24-Parganas, West Bengal

Fig. 2 : Effect of arsenic contamination **Source :** *Sanyal (2005)*

to be the highest in Bangladesh, followed by West Bengal, India (Chowdhury *et al.,* 2000; Chowdhury *et al.,* 2001). The scale of the problem is grave and unprecedented, covering a geographic area of 0.173 million square kilometer, while exposing at least 36 million people in the Bengal delta basin to risk (Das *et al*., 1995; BGS and DPHE, 2001). The widespread arsenic contamination in groundwater in different parts of West Bengal, distributed over 111 blocks, located primarily in five districts adjoining the river Bhagirathi, as well as the contiguous districts in Bangladesh, is of great concern (Sanyal and Nasar, 2002). Even beyond the Bengal delta basin, the widespread arsenic contamination in groundwater above the permissible limit ($50\ \mu g\ l^{-1}$; WHO, 2001) has also been detected in several places in the country (Table 1, Figure 1), for instance at Chandigarh (1976), Nepal (2001), Bihar (2002), Uttar Pradesh (2003), Jharkhand (2003-2004) (Sanyal and Dhillon, 2005) and Punjab (2006-2007).

Two major hypotheses, both of geogenic origin, have been proposed to account for such widespread arsenic contamination in the groundwater in parts of West Bengal and Bangladesh confined within the delta bound by the rivers Bhagirathi and Ganga-Padma. Of these two hypotheses, namely the arsenopyrite oxidation hypothesis (Mandal *et al*., 1996) and the ferric oxyhydroxide reduction hypothesis (Bhattacharya *et al*., 1997; Nickson *et al*., 1998), the latter is more consistent with the experimental observations reported for the aquifer sediments and water of the Bengal delta basin (Sanyal, 1999; Sanyal and Nasar, 2002). According to this hypothesis, an anoxic condition of the aquifer causes arsenic mobilization from arsenic-bearing sediments into the groundwater aquifer. The maintenance of such anoxic condition is proposed to be facilitated by the widespread practice of wetland paddy cultivation in the affected belt.

3. Natural abundance

Dissolved arsenic concentrations in natural waters (except groundwater) are generally low, except in areas characterized by geothermal water and/or mining activities. The sedimentary rocks generally have higher arsenic content (Table 2) than do igneous and metamorphic rocks, while suspended and bottom sediments in most aquatic systems contain more arsenic (Table 2) than most natural waters (Table 3) (Welch *et al*., 1988; ICAR, 2003). The capacity to retain arsenic is primarily governed by the sediment grain-size and the presence of surface coating composed of clays, clay-sized iron and manganese oxides and organic matter.

Arsenic held by solid phases within the sediments, especially iron oxides, organic matter and sulphides may constitute the primary arsenic sources in groundwater under conditions conducive to arsenic release from these solid phases. These include abiotic reactions (oxidation/reduction, ion exchange, chemical transformations) and biotic reactions (microbial methylation) (Mok and Wai, 1994).

4. Arsenic contamination in groundwater in the Bengal Delta Basin

The groundwater arsenic (As) concentration (50 – 1600 mg/l), reported from the affected areas of West Bengal, are several orders of magnitude higher than the stipulated Indian standard for the permissible limit in drinking water (50 mg/l, which is also the maximum acceptable concentration, MAC, for drinking water in Bangladesh, India and several other countries), as well as the WHO guideline value (10 mg/l) (Das *et al*., 1995; PHED, 1993; CGWB, 1999; RGNWM, 2001).

Table 2: Arsenic concentration in rocks and some other materials

Type of rock/materials	Arsenic content (mg As/kg)
1. Rocks	
Igneous	
Ultrabasic:	
Peridotite, dunite, serpentine	0.3-15.8
Basic:	
Basalt (extrusive)	0.18-113
Gabbro (intrusive)	0.06-28
Intermediate:	
Latite, andesite, trachyte (extrusive)	0.5-5.8
Diorite, granodiorite, syenite (intrusive)	0.09-13.4
Acidic:	
Rhyolite (extrusive)	3.2-5.4
Granite (intrusive)	0.18-15
Metamorphic rocks	
Quartzite	2.2-7.6
Slate/phyllite	0.5-143
Schist/gneiss	0.0-185
Sedimentary rocks	
Marine	
Shale/claystone (nearshore)	4.0-25
Shale/claystone (offshore)	3.0-490
Carbonates	0.1-20.1
Phosphorites	0.4-188
Sandstone	0.6-9.0
Nonmarine	
Shales	3.0-12
Claystone	3.0-10
2. Coal	Upto 2000
3. Crustal average	2.0

Source: *Compiled from different sources.*

Table 3: Arsenic concentrations in water other than groundwater

Source	Arsenic (µg As/l)
Rainwater and snow	<0.002-0.59
Rivers	0.20-264
Lakes	0.38-1.00
Sea water	0.15-6.00
Ponds (West Bengal, India)	4-70
Canals (West Bengal, India)	40-150

Source: *Welch et al. (1988) and ICAR (2003)*

Further, the arsenic concentration in alluvial aquifers of Punjab varied from 4 to 688 µg/l (Hundal *et al.,* 2007). In groundwater of Zone I, comprising Gurdaspur, Hoshiarpur, Nawanshahr, and Ropar districts, As varied from 4 to 42 µg/l. The concentration of As in groundwater of Zone II, comprising Amritsar, Tarn Taran, Jalandhar, Kapurthala, Ludhiana, Patiala, Mohali, Barnala, and Moga districts, varied from 10 to 43 µg/l. In the arid southwestern zone (Zone III), comprising Sangrur, Mansa, Faridkot, Muktsar, Bathinda, and Ferozepur, As concentrations varied from 11 to 688 µg/l. According to the safe limit of 10 µg As/l, only 3% groundwater samples from Zone I and 1% from Zone II were fit for dinking purposes with respect to As concentration. In Zone III, all water samples had As concentrations greater than the safe limits and thus were not suitable for drinking purposes (Aulakh *et al.*, 2009; Sanyal *et al.*, 2012).

In West Bengal, the presence of arsenic in groundwater in concentrations exceeding maximum acceptable concentration was first detected in 1978, while the first case of arsenic poisoning in humans was diagnosed at the School of Tropical Medicine in Calcutta in 1983 (Acharya, 1997). The effect of ingestion of inorganic arsenic in drinking water and the health effects in adults has also been well established (Guha Mazumdar *et al.*, 1998). The main focus of attention, until recently, has been exclusively on arsenic contamination in groundwater-derived drinking water.

However, since groundwater is also used extensively (more than 90%) for crop irrigation in the arsenic belt of West Bengal, the possibility of a build-up of arsenic concentration in agricultural soils and agronomic produce was anticipated. Indeed, arsenic uptake by crop plants grown in soils contaminated with high concentration of arsenic, and irrigated with such arsenic contaminated groundwater has been reported by several workers (ICAR, 2001; ICAR, 2003; Ghosh *et al.*, 2004; Abedin *et al.*, 2002; Adak *et al.*, 2002; Duxbery *et al.*, 2003; Sanyal and Dhillon, 2005; Das *et al.*, 2013). Such findings call for an immediate attention since what remains essentially a *point* and fixed source of arsenic contamination as for drinking water (e.g., a tube-well discharging contaminated water), may well become a *diffuse* and uncertain source of contamination when arsenic finds its way into the food web, accompanied with possible biomagnification up in the food chain (Sanyal and Dhillon, 2005). This assumes added significance in view of the reported finding of higher (than permissible) level of arsenic in the urine samples of some people having no history of consuming arsenic contaminated drinking water (Dr. D.N. Guha Mazumdar, by private communication). Interestingly, the surface water bodies, located in the affected belt, have remained largely free of arsenic. This tends to suggest that the soil, which receives arsenic-contaminated water, acts as an effective sink to contain the toxin (as stated earlier), thereby preventing the surface run-off to carry it to the adjoining water systems (Sanyal, 2005).

5. Guideline value of maximum arsenic concentration

As mentioned briefly earlier, the World Health Organization (WHO)-recommended provisional guideline value of *total* arsenic (As) concentration in drinking water is 0.01 mg As/l since 1993 (WHO, 1993), mainly because lower levels preferred for protection of human health are not reliably measurable on a large scale. However, the National Standard for maximum acceptable concentration (MAC) of arsenic in drinking water is 0.05 mg As /l in several countries including India and Bangladesh based on an earlier WHO (1971) advice.

The proposed new standard value of 0.005 mg As/l is under consideration (WHO, 2001). This is due mainly to the fact that inorganic arsenic compounds are classified in Group 1 (carcinogenic to humans) on the basis of adequate evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals (IARC, 1987). Adequate data on the carcinogenicity of organic arsenic have not been generated. The joint FAO/WHO Expert Committee on Food Additives (JECFA) set a provisional maximum tolerable daily intake (PMTDI) of inorganic arsenic as 0.002 mg As/kg of body weight for humans in 1983 and confirmed a provisional tolerable weekly intake (PTWI) as 0.015 mg As/kg of body weight in 1988 (FAO/WHO, 1989). Such guideline values for soil, plant and animal systems are not available.

6. Health implications of arsenic poisoning

Arsenic is a widely occurring toxic metal in natural ecosystems. As small as 0.1 g of arsenic trioxide can prove lethal to humans (Jarup, 1992). Early symptoms of arsenic poisoning include skin disorders, weakness, languor, anorexia, nausea and vomiting with diarrhoea or constipation (Figure 2). With the progress of poisoning the symptoms attain more characteristic features, which include acute diarrhoea, oedema (especially of the eyelids and ankles), skin pigmentation, arsenical melanosis and hyperkeratosis, enlargement of liver, respiratory diseases and skin cancer. In severe cases, gangrene in the limbs and malignant neoplasm are also observed (Mandal *et al.*, 1996). "Bell Ville Disease" (typical arsenic induced cutaneous manifestations among the people of Bell Ville) in Argentina, "Black Foot Disease" in Taiwan and "Kai Dam" disease in Thailand are well established as health disorders due to arsenic poisoning (Sanyal, 1999). As a matter of fact, the hair, nail, skin-scale and urine samples of a large number of people residing in the affected belt of West Bengal (India) and Bangladesh, have been analyzed by several workers. Many of these samples had arsenic loading more than the corresponding toxic levels (Sanyal and Dhillon, 2005; Rattan *et al.*, 2009).

7. Chemistry of arsenic in groundwater-soil environment

Arsenic in groundwater is generally present as dissolved, deprotonated/protonated oxyanions, namely arsenites ($As^{III}O_3^{3-}$; $H_n As^{III}O_3^{(3-n)-}$, with n = 1,2) or arsenate ($As^VO_4^{3-}$, $H_nAs^VO_4^{(3-n)-}$, with n = 1,2), or both, besides the organic forms. The toxicity of arsenic compounds in groundwater/soil environment depends largely on its oxidation state, and hence on redox status and pH, as well as whether arsenic is present in organic combinations. The toxicity follows the order: arsine [AsH_3; valence state of arsenic (As): -3]>organo-arsine compounds >arsenites (As^{3+}form) and oxides (As^{3+} form) > arsenates (As^{5+} form) > arsonium metals (+1) > native arsenic metal (0). The arsenites are much more soluble, mobile, and toxic than arsenates in aquatic and soil environments. At pH 6-8, in most aquatic systems, both $H_2As^VO_4^-$ and $HAs^VO_4^{2-}$ ions (pentavalent arsenic forms) occur in considerable proportions in an oxidized environment (redox potential, E_h= 0.2-0.5V), while the arsenous acid, $H_3As^{III}O_3$, is the predominant species (trivalent arsenic form) under reduced conditions (E_h = 0-0.1V) (Sadiq, 1997; Sanyal and Nasar, 2002, Ghosh *et al.*, 2004).

The solubility, mobility, bioavailability and hence toxicity of arsenic in soil-crop system also depends on its chemical form, primarily the oxidation state (Woolson, 1977; Sun and Doner, 1998). The inorganic forms of arsenic in soils and sediments include arsenites and arsenates. The organic forms, namely dimethylarsinic acid or cacodylic acid, which on reduction (e.g., in anoxic soil conditions) forms di- and trimethyl arsines, are also present (Woolson, 1977). Under oxidizing aerobic conditions (characterized by high E_h), arsenic acid species and the arsenate oxyanions ($H_3AsO_4^o$, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) are stable in soil environment (Welch *et al.,* 1988), whereas under mildly reducing conditions (such as one encounters in flooded paddy soils with E_h = 0-0.1V), and a pH range of 6 to 8, arsenous acid species and arsenite oxyanion species ($H_3AsO_3^0$, $H_2AsO_3^-$, $HAsO_3^{2-}$) are the stable forms (Sanyal, 1999). Furthermore, it has been recognized that As (III) is more prevalent in soils of neutral pH range (and in most groundwater), as in the soils of the affected belt of West Bengal, India and Bangladesh, than otherwise thought, and hence is of concern. This is primarily because As (III) exists as a neutral, uncharged molecule, namely arsenous acid, $H_3AsO_3^0$ (pK_a= 9.2), at the pH of neutral soils and most natural groundwater as one would expect based on the Henderson's equation (Sanyal, 1999), and is thus less amenable to retention by the charged mineral surfaces in soils and sediments.

However, it ought to be emphasized that groundwater or soil solution, which is subject to affluxes and influxes, as well as circulation and also to man-made perturbations of groundwater due to its withdrawal, can not be expected to remain in thermodynamic equilibrium, it being very much of an open system (thermodynamically speaking). Thus, more often than not, the ratio of concentrations of arsenic species, namely the ratio, [As (III)/As (V)], in field soils does *not* quite agree with the ones computed from the observed redox potential (E_h) and the application of the Nernst's equation (at 25^0C) to the equilibrium redox reaction, namely

$$AsO^3_{4-} + 2H^+ + 2e = AsO_3^{3-} + H_2O,$$

$$Eh \cong E^oh - 0.0295 \log \frac{[AsO_3^{3-}]}{[AsO_4^{3-}]} - 0.059pH \qquad (1)$$

It is evident from equation (1) that the proportion of As (III), and hence soluble arsenic level in soil, should increase substantially with diminishing E_h and increasing pH. Furthermore, at a high pH, the OH^- ion concentration would increase, causing displacement of As (III) and As (V) species from their binding sites through competitive ligand exchange reactions (Sanyal, 1999; Sanyal and Nasar, 2002; Sanyal *et al.*, 2009).

The dependence of arsenic sorption on pH of the sorption medium is governed largely by the nature of the soil colloidal fraction (Majumder and Sanyal, 2003). A fall of arsenate adsorption was noted with increasing pH, but only at lower arsenate concentrations, which got reversed at a higher arsenate equilibrium concentration. This trend was explained in terms of the varying electrostatic potential of the variable-charge soil colloidal surfaces with pH, solubility product principles, and buffering action of the arsenic salt used (Majumder and Sanyal, 2003).

There have been both direct and indirect evidence to suggest that arsenic (and selenium) is held in soils and sediments by oxides (e.g., of Fe, Al, Mn) through the formation of inner-sphere complexes *via* ligand exchange mechanism (Woolson, 1977; Livesey and Huang, 1981; Majumder and Sanyal, 2003). This is shown as follows (Hingston *et al.,* 1974; Sanyal *et al.*, 2009).

$$M - OH + H_2O \rightleftharpoons M - OH_2^- + OH^-$$

$$M - OH_2^+ + H_2AsO_4^- \rightleftharpoons M - O^+H_2 \ldots\ldots H_2AsO^-_4 \text{—(2)}$$

Or

$$M - OH + H_2AsO_4^- \rightleftharpoons [M - O^+ - H \ldots . H \ldots HAsO_2^{2-}]$$

$$\rightleftharpoons M - HAsO^-_4 + H_2O$$

However, the non-specific adsorption (through electrostatic mechanism) of arsenic also occurs at pH values below the point of zero charge (PZC) for a given adsorbent (Sanyal *et al.*, 2009, Rattan *et al.*, 2009; Sanyal *et al.*, 2012). As shown in the reaction scheme 2, the above stated ligand exchange tends to increase the negative charge of the soil colloidal fraction, for instance, of iron oxides, and thus push the point of zero-charge (PZC) of the arsenic laden soil to lower pH. Indeed, this was shown (Ghosh *et al.,* 2003) to be the case in an incubation experiment wherein arsenic loading of soils from the affected site was found to shift the PZC to lower pH compared to the untreated soil, with concomitant increase in the negative magnitude of the variable-surface charge and the surface potential of the corresponding soil colloidal fraction.

8. Selected findings in soil-crop system

Arsenic loading in soils of West Bengal

Some of the research studies, conducted at the selected affected areas, revealed that the total and Olsen extractable (i.e., 0.5M $NaHCO_3$, pH 8.5–extractable arsenic which constitutes the soil arsenic pool amenable to plant uptake) arsenic varied from 8.4 to 24.3 mg/kg and from 2.90 to 15.8 mg/kg, respectively (ICAR, 2001; ICAR, 2003; SWID, 2003), in the given affected soils of West Bengal. The soil arsenic contents of these areas were generally higher than those reported for the soils of several other countries like Argentina, China, Italy, Mexico, France, Australia, etc. (Sanyal and Nasar, 2002).

Inorganic soil arsenic from the affected soils was also fractionated into different soil arsenic pools, namely water soluble As (Ws–As), arsenic associated with Al compounds in soil, the so-called aluminium-bound As (Al-As), iron-bound As (Fe–As) and calcium-bound As (Ca–As), by following the sequential extraction methodology. The findings suggested that these inorganic soil As pools fell in the order: Ws-As < Al-As < Ca-As < Fe-As (ICAR, 2001; SWID, 2003). In particular, the Fe-As fraction contributed 45% to 74.7% towards the total soil arsenic sequential sum (ICAR, 2001; SWID, 2003; Ghosh *et al.*, 2003).

Interaction of arsenic with organics in soil system

As mentioned earlier, soil acts as an effective sink of arsenic present in the contaminated groundwater used for irrigating the crops. The soil organic fractions including humic acid (HA) and fulvic acid (FA) behave as effective accumulators of toxic heavy metals, following the formation of metal-humate complexes (chelates) with different degrees of stability (Datta *et al.*, 2001; Mukhopadhyay, 2002; Mukhopadhyay and Sanyal, 2004; Ghosh *et al.*, 2012). Besides, soil clays, aluminum oxides, iron oxides, especially the amorphous iron and aluminium oxides in soil also influence the arsenic retention by soils, soil minerals and sediments (Sanyal, 1999; Carey *et al.*, 1996; Manning and Goldberg, 1997). The stability constant (log K) of the complexes formed by the soil HA/FA with arsenic in the selected contaminated soils of West Bengal suggested that organo-arsenic complexes were quite stable, even in the presence of competing oxyanions such as phosphate and nitrate (Mukhopadhyay and Sanyal, 2004). Thus, improving the soil organic matter stock in the tropical soils of the arsenic-affected belt of West Bengal (which are relatively poor in native organic matter) by way of adopting the appropriate management practices (such as recycling of crop residues, incorporation of organic manure, etc.) is necessary for facilitating arsenic retention in the soils of arsenic–affected belt

(Mukhopadhyay and Sanyal, 2004). Indeed, the use of FYM, compost, vermicrompost, neem cake, poultry manure, etc., has proved quite effective in minimizing the labile arsenic pool in soil and crop uptake of arsenic (Sanyal, 2005; Ghosh *et al*., 2012).

Interaction of arsenic with phosphorus

Phosphorus (P) is one of the essential major plant nutrients for plant growth. Because arsenic and P are both placed in Group Vb of the Periodic Table, the interaction of arsenic (As) and phosphorus in soil-plant system is an important issue in respect of arsenic mobilization. Indeed the indications are that these oxyanions would not be adsorbed independently in mixtures, but rather would tend to compete for some portion of the same type of adsorption sites (Sanyal *et al*., 2009).

Several workers showed that the presence of phosphate caused a reduction in arsenate adsorption, and that the reduction was much greater for the competitive effects of arsenate on phosphate adsorption by soil minerals, although a large variation in the degree of competition between these two oxyanions has also been reported (Kuo and McNeal, 1984; Sadiq, 1997; Manning and Goldberg, 1997; Jackson and Miller, 2000; Melamed *et al*., 1995; Mukhopadhyay *et al*., 2002;).

Arsenic in soil-plant system

Several workers have reported accumulation and transformation of arsenic by a number of plant species grown in the arsenic affected areas. These crops (such as elephant-foot-yam, green gram, cowpea, sesame, groundnut, etc.) tended to show a build-up of arsenic in substantial quantities in different plant parts (ICAR, 2001; ICAR, 2003; SWID, 2003). Indeed, pointed gourd, a vegetable creeper plant, has shown considerable arsenic loading when cultivated in the soils of West Bengal (Panda and Das, 2001 reported by ICAR, 2001). A number of other vegetables, namely cauliflower, tomato, bitter gourd were also noted to accumulate arsenic in their economic produce (ICAR, 2001; ICAR, 2003; SWID, 2003; Ghosh *et al*., 2004; MoWR, 2004). The distribution of arsenic content in plant parts generally followed the order: root > stem>leaf > economic produce.

Reduction of arsenate to more toxic arsenite is facilitated by lowering of redox potential (E_h) which is encountered under anoxic soil conditions, with arsenite being more soluble and mobile than arsenate. Thus, rice plant is rather susceptible to arsenic toxicity since it is grown under submerged soil conditions (low E_h) (Sanyal, 1999; Sanyal and Nasar, 2002; Mukhopadhyay, 2002). Thus, the total arsenic loading of rice crop was to the tune of 10 mg/kg and even more at 14% moisture level in the selected districts of Bangladesh (Duxbery *et al*., 2003; Das *et al*., 2013). Further, the processing of rice (i.e., parboiling and milling, etc.) was found to increase the arsenic loading in rice for both the traditional and the high yielding cultivars. The toxicity of arsenic species in plant body is reported to follow the order: Arsine (AsH_3) > As^{3+} > As^{5+}> MMA (Monomethyl arsonic acid)> DMMA (Dimethyl arsinic acid) (NRCC, 1978).

Pot culture experiments were conducted by Das *et al.* (2013) using graded doses of arsenic (As) applied to rice plant in order for ascertaining the As toxicity symptoms in rice. The As accumulation by the plant parts generally followed the order: root > stem > leaf > economic produce. Yield reduction of 80.8% was observed in treatment applying more than 60 mg As kg^{-1}. The arsenic toxicity symptoms in leaf and root were observed with treatment above 40 mg As kg^{-1}, while the symptoms were apparent in economic produce above 60 mg As kg^{-1}. The phytotoxicity threshold levels were observed with yield reduction to 55.5% in tillering and 54.8% at harvesting. In field experiments of rice-green manure–rice cropping sequence, no toxicity symptoms developed but a greater extent of As accumulation in rice crops was observed. The application of green manure did *not* significantly reduce As accumulation in the succeeding rice crop. The As accumulation and translocation factors in both these experiments revealed the following order of As accumulation: root > stem > leaf > economic produce (Das *et al*., 2013).

Transport studies on aqueous arsenic (As) in selected As affected and unaffected soils of West Bengal were conducted by Das *et al.* (2014) with the help of double chambered columns in the laboratory. In the vertical column study, the sigmoid shape of the breakthrough curves (BTCs) suggests hydrodynamic dispersion whereas the inflextion of BTCs at a much less relative concentration indicates retention of As in the affected soils. In the horizontal column study, the affected soils showed lower mechanical filtration capacity, solute permeability and higher reflection coefficient, thereby indicating a greater degree of As retention in these soils. The frictional coefficients for soil-water-solute derived from the horizontal flow also indicate As retention by the affected soils. The As retention capacity of these soils was attributed to the greater clay content of illitic and kaolinitic nature, organic matter, specific surface area, amorphous iron and aluminum content of the given (affected) soils.

Furthermore, screening of 200 rice genotypes showed a large variation of arsenic accumulation in grain. Most of the high yielding cultivars examined contained more than 0.6 mg/kg of grain. No significant correlation was found among the pattern of arsenic uptake by root, shoot and grain of the 200 rice lines examined. Initial analysis revealed that arsenic content in grain is controlled by more than one gene. It has also been found that crops like potato, pumpkin and sesame accumulate less arsenic than do others (BCKV Arsenic Research Group, Unpublished work).

On storing the arsenic contaminated groundwater (from a shallow tube-well, STW) in a pond, there was a gradual lowering (on standing) of arsenic loading of the stored pond water, while its progressive build-up in the corresponding sediment samples (MoWR, 2004). Such decrease of arsenic content in the stored water might have arisen from the sedimentation of arsenic from the water to the pond sediment which obviously increases the arsenic loading in the latter. The dilution of the stored water by rainfall during the wet season (July to September) further decreased the contamination in the water. This opens up the possibility of conjunctive use in agriculture of surface and groundwater during the *lean period* as a potential remedial option (MoWR, 2004).

9. Hyper-accumulation *vis-v̋-vis* detoxification of arsenic by plants / microbial species

The reported hyper-accumulation of arsenic (As) from the contaminated soils by the brake-fern, *Pteris vittata,* and its subsequent translocation into the above-ground biomass suggests that the plant-accumulated arsenic was present almost entirely in the toxic inorganic forms with the proportion of highly toxic As (III) being in fact much greater in the plant body than that of the less toxic As (V) form, as compared to the distribution of these two forms in the contaminated soil in which the fern grows (Ma *et al.*, 2001). Conversion of the plant-accumulated inorganic forms of the toxin to non (or less)–toxic organometallic forms by plant metabolism would certainly aid the detoxification process (Sanyal and Nasar, 2002).

A scan of literature reveals a number of plant/microbial species, known for arsenic accumulation/or as bio-indicator, which can effectively remove arsenic (and other heavy metals) from the aquatic system, for instance, to the tune of 170 and 340 mg As/g dry weight of water hyacinth in its stem and leaves, respectively (Chigbo *et al.*, 1982), when grown in a pond containing 10 mg As/dm^3. However, such accumulated arsenic in water hyacinth (*Eichornia crassipes*) is also liable to leaching out in the water body, particularly so on decomposition of such aquatic weed. Consequently, appropriate precaution has to be exercised while interpreting the arsenic status of aquatic environment by water hyacinth accumulation (Low and Lee, 1990).

A number of microbial species (e.g., the bacterial species, namely *Proteus* sp., *Escherichia coli*, *Flavobacterium* sp.; *Corynebacterium* sp. and *Pseudomonas* sp., the fungus, namely *Candida humicola;* the freshwater algae, namely *Chlorella ovalis. Phaepdactuylum tricornutum. Oscillatoria rubescens*) have been reported to possess varying degrees of arsenic accumulating abilities (Sanyal and Nasar, 2002).

Several weed species normally found along with crops like rice, potato, jute, mustard, etc., growing on arsenic contaminated soils (2-14 mg As/kg soil) and subjected to irrigation (given to the desired crops) with arsenic contaminated groundwater, were noted to accumulate considerable amounts of arsenic in their biomass. Table 4 demonstrates the extent of such arsenic accumulation by these weed species (Das *et al.*, 2005).

Table 4: Arsenic content of different weed flora in the existing crop fields of selected arsenic contaminated area of West Bengal

Weeds	Arsenic content (mg As kg^{-1})	
	Stem	Leaf
Ludwigia parviflora	3.12	-
Enhydra sp.	12.3	-
Filmbristylis sp.	14.1	28.1
Eleusine indica	2.40	-
Ageratum conyzoides	4.50	14.1
Croton sparsiflora	12.2	10.4
Lantana camara	8.40	10.2
Vitis trifolia	4.30	7.91

Source: Das *et al.*, 2005

However, it is worth noting in this context that such accumulation of arsenic does *not* necessarily lead to its detoxification *per* se (Sanyal, 1999; Sanyal and Dhillon, 2005) unless the plant- accumulated toxin is effectively detoxified within the plant body by its metabolic processes. For this, a systematic search for phyto-accumulating or phyto-excluding plant species is necessary.

10. Remedial options at a glance

a. Optimum conjunctive use of ground and surface water [e.g., use of harvested rainwater during the lean period].

b. Development/identification of suitable low arsenic accumulating high yielding crops/ varieties suitable for arsenic contaminated areas.

c. Irrigation with pond-stored groundwater-decontamination being facilitated by rainfall and sedimentation.

d. Recharge of groundwater resource with harvested rainwater, free of arsenic.

e. Enhancing the water use efficiency (through optimum water management) for groundwater irrigation, especially for summer (*boro*) rice.

f. Preferring low-water requiring, farmer-attractive cropping sequences (especially for the lean period).

g. Increased use of FYM and other manures plus green manure crops, inclusion of pulses/other legumes in the cropping sequences, as well as application of appropriate amendments (zinc/iron salts as and wherever applicable).

h. Cost-effective phytoremediation options.

i. Creation of general awareness: Mass campaigning, holding of farmers' day, field demonstrations, socioeconomic factors.

11. Future research thrust

In addition to the remedial options to address the issue of the arsenic toxicity in the food-web, further intensive research is the need of the day in order to contain the toxic effect of the entry of arsenic in the human food-chain. The projected thrust areas are the following, among others:

- Speciation of arsenic in various substrates for ascertaining its *net* toxicity, release mechanism, spatial resolution, chemical transformations and hence its toxicity, bioavailability and impact on human health.
- Elucidation of mechanism for microbial transformations of arsenic on soil components-Transformation of toxic species to less toxic forms or production of volatile species of the toxins.
- Advanced knowledge generation regarding speciation of arsenic within the plant biomass and possible relation to rhizosphere speciation and biochemistry, and the chemical structure of metal-binding proteins.
- Effective remediation and waste management strategies.
- Risk assessment.
- Soil chemists ought to work in close association with soil biochemists, geochemists, mineralogists and plant physiologists, using synchrotron-based techniques as well as genomic, proteomic and bioinformatics approaches in order to produce better metal-accumulating plants, thereby facilitating the remediation efforts.

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