



Arsenic contamination in Ballia and phytoremediation

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Abstract

Over thousands of years, Arsenic (As) has been washing down from the Himalayas with the Ganga water as sediment, sinking in and mixing with groundwater. In the plains, this As has been leaching into the ground. Some As occurs naturally in groundwater, within limits not harmful. It remained within permissible limits and did no harm till around the 1970s when, concerned over deaths in the Gangetic belt caused mainly by the unhygienic pattern of water consumption and poor sanitary conditions, the Indian government and UNICEF sank millions of tubewells. After 1970, indiscriminate drawing of groundwater resulted in water table sinking and increasing As content. In India, seven states namely, West-Bengal, Jharkhand, Bihar, Uttar Pradesh in the flood plain of Ganga River; Assam and Manipur in the flood plain of Brahmaputra and Imphal rivers and Rajnandgaon village in Chhattisgarh state have so far been reported affected by As contamination in groundwater above the permissible limit of 50 µg/L. People in these affected states have chronically been exposed to As drinking arsenic contaminated hand tube-wells water. With every new survey, more As affected villages and people suffering from arsenic related diseases are being reported, and the problem resolving issues are getting complicated by a number of unknown factors. It is now generally accepted that the source is of geological origin and percolation of fertilizer residues may have played a modifying role in its further exaggeration. Identification of parental rocks or outcrops is yet to be recognized, including their sources, routes, transport, speciation and occurrence in Holocene aquifers along fluvial tracks of the Ganga-Brahmaputra-Barrak valley. It is reported that the contaminated waters are enriched in Fe, Mn, Ca, Mg, bicarbonates, and depleted in sulphate, fluoride, chloride; pH ranged from 6.5 to 8.0; redox condition usually in reducing; high an organic matter content; lodged mostly in sand coatings, or sorbed on clays and organic matters. It has been proved that As has affinity with iron in groundwater both positively and negatively, depending upon the condition. This gives a positive hope of devising *in situ* remediation of the problem of As contamination by removal of Fe from groundwater before withdrawal. Varieties of As removal devices have been developed, based on different working principles, and have been extended to fields. Many of those could not produce satisfactory performance due to sludge disposal problems. Among the various removal technologies, lime softening and iron co-precipitation have been reported to be the most effective removal technologies, and observed running satisfactorily, where operation and maintenance problems were taken care of by public-private partnership. The available As removal technologies require refinement to make them suitable and sustainable for their large scale effective uses. Alternative removal technology i.e. phytoremediation is ecofriendly and cost effective.

Key words- Arsenic, contamination, underground water, phytoremediation

Introduction

Arsenic (**As**) is a common, naturally occurring drinking water contaminant that originates from **As**-containing rocks and soil and is transported to natural waters through erosion and dissolution. It is followed by subsequent leaching and runoff. It can also be introduced into soil and groundwater from anthropogenic sources. There are many factors which control **As** concentration and transport in groundwater, which include: Arsenic speciation, Redox potential (Eh), adsorption or desorption, precipitation or dissolution, pH, presence and concentration of competing ions, biological transformation, etc. The **As** species, adsorption and desorption reactions, Eh, pH and solid-phase dissolutions and precipitations may vary from aquifer to aquifer that depend upon the geological settings, geo-chemistry and geo-environmental conditions of an aquifer. Arsenic occurs with many minerals, usually in combination with sulfur and metals, but also as a pure elemental crystal. **As** is a metalloid and has various allotropes, but only the gray form is important to industry. Arsenic is typically found in the soil in organic forms as Arsenate, Arsenite, Dimethyl arsenic acid and Monomethyl arsenic acid; in inorganic forms as Arsenate or **As** (V) and Arsenite **As** (III). Arsenate prevails under aerobic conditions, is less toxic and less mobile than Arsenite, due to stronger soil sorption. The main sources of **As** contamination are Mine waste (primarily sulfide, iron and tin) Tanneries, Metal smelters, and Geothermal activities. **As** has been used in the following paint pigments, Insecticides, Herbicides, Defoliants, Metal alloys-car batteries, etc.

Arsenic reports in India

In India, since the groundwater arsenic contamination was first surfaced from West-Bengal in 1983, a number of other States, namely; Jharkhand, Bihar, Uttar Pradesh in flood plain of the Ganga River; Assam and Manipur in flood plain of the Brahmaputra and Imphal rivers, and Rajnandgaon village in Chhattisgarh state have chronically been exposed to drinking arsenic contaminated hand tube-wells water above permissible limit of 50 µg/L. Many more North-Eastern Hill States in the flood plains are also suspected to have the possibility of arsenic in groundwater. Even with every additional survey, new arsenic affected villages and people suffering from arsenic related diseases are being reported. All the arsenic affected river plains have the river routes originated from the Himalayan region. Whether or not the source material has any bearing on the outcrops is a matter of research, however, over the years, the problem of groundwater arsenic contamination has been complicated, to a large variability at both the local and regional scale, by a number of unknown factors.

Since groundwater arsenic contamination was first reported in year 1983 from 33 affected villages in four districts in West-Bengal, the number of villages has increased to 3417 in 111 blocks in nine districts till 2008 in West Bengal alone. In 1999, the arsenic groundwater contamination and its health effects in Rajnandgaon district of Chattisgarh state were also detected. In 2002, two villages, Barisban and Semaria Ojhapatti, in Bhojpur district, located in the western part of the Bihar state, were reported having contamination exceeding 50µg/L. As of 2008, out of 38 districts of Bihar, 57 blocks from 15 districts having total population

nearly 10 million have been reported affected by arsenic groundwater contamination above 50µg/L. During 2003, 25 arsenic affected villages of Ballia district in Uttar Pradesh and people suffering from skin lesions came into limelight. During 2003-2004, the groundwater arsenic contamination and consequent suffering of hundreds of people were reported from 17 villages of the Sahibgunj district of Jharkhand state, in the middle Ganga plain. In 2004, arsenic concentration was also reported from Assam in pockets of 2 districts. In 2007, Manipur state, one of the seven North-Eastern Hill States, had also come into limelight of arsenic contamination in groundwater. Many more North-Eastern Hill States in the flood plains are also suspected to have the possibility of arsenic in groundwater (Singh, 2006; Mukherjee *et al.*, 2006; Michael and Voss, 2008).

Sources of Arsenic in Ganga–Brahmaputra Aquifers

There is no evidence regarding the natural emission of As in the Ganga–Brahmaputra plains so far. However, the release of As, by the natural processes in groundwater, has been recognized, from the Holocene sediments comprising sand, silt and clay (Bhattacharya *et al.*, 1997; McArthur *et al.*, 2004) in parts of the Bengal Delta Plains (BDP), West Bengal and in the Gangetic plains of Bihar. Several isolated geological sources of As have been recognized, viz. Gondwana coal seams in Rajmahal basin (200 mg/kg of As), Bihar mica-belt (0.08–0.12% of As), pyrite-bearing shale from the Proterozoic Vindhyan range (0.26% of As), Son valley gold belt (2.8% of As) and Darjeeling Himalayas belt (0.8% of As) (Bhattacharya *et al.*, 2002; Acharyya *et al.*, 1993; Acharyya *et al.*, 1999). The contaminated aquifers are of Quaternary age and comprise micaceous sand, silt and clay derived from the Himalayas and basement complexes of eastern India. These are sharply bound by the River Bhagirathi-Hooghly (tributary of the River Ganges) (Bhattacharyya *et al.*, 2005) in the west, the rivers, Ganges and Padma in the north, the flood plain of the River Meghna (tributary of the River Padma), and the River Yamuna in the northeast (Acharyya *et al.*, 2000).

The actual source of groundwater arsenic contamination, in the Ganga–Brahmaputra basin, is yet to be established. The sources of arsenic are natural or may partly stem from anthropogenic activities like intense exploitation of groundwater, application of fertilizers, burning of coal and leaching of metals from coal-ash tailings. The hypotheses about the sources of arsenic in the Ganga-Brahmaputra Aquifers are as follows:

- Arsenic, transported by the River Ganges and its tributaries from the Gondwana coal, seams in the Rajmahal trap area located at the west of the basin can be of the order of 200 ppm. (Saha, 1991).
- Arsenic is transported by the north Bengal tributaries of Bhagirathi and Padma from near the Gorubathan base-metal deposits in the eastern Himalayas (Ray, 1999).
- Arsenic is transported with the fluvial sediments from the Himalayas (McArthur *et al.*, 2004). This is the most accepted hypothesis at present.

Arsenic in Ballia District of Uttar Pradesh

Uttar Pradesh State (UP) is located at north of India bordering on Nepal, Geo- graphical area of which is about 4700 km², where two big rivers are running from the northwest to the south- east. The former is the Ghaghara River flowing down from the arsenic affected *Terrai* plane, and the latter is the Ganges River. The arsenic contamination in UP State was first recognized in 2003 at Ballia District, where both of the Ghaghara and the Ganges are joining. Arsenic-contaminated tubewells, water is detected in the 20 Districts in UP State by UP government under the assistance of UNICEF. The government survey was, however, performed only for the government tubewells (GTWs), and private tubewells (PTWs), numerous compared with GTW, were not checked at all. In regard to arsenocosis patients, the number of patient is unknown yet, because the medical examination has not been executed until now. Sources revealed that arsenic was first reported in drinking water of Ballia in 2003. Survey carried out by U P Jal Nigam (2004), in Ballia, revealed the concentration of As was found above prescribed threshold level. Ballia is located in eastern most part of UP with shared in 17 blocks. The Ganga is main river basin and also drained with Ghagra on North and Choti Sargu in the South. Agriculture is the main activity (72%) because of poverty (44%) and low literacy (58%). For irrigation purpose people depend on groundwater, tubewell and number of 'Tal' and canals like 'Surah tal', Sikanderpur Tal', etc. High As concentration has been in all blocks in groundwater, includes- Belthara Road, Nagara, Rasara, Chilkahar, Maniyar, Sohaon, Dubhad, Bansdeeh, Revati, Beriya, Belhari, Pandah, Navanagar, Beruarbari, Garhwar and Muralichapra. The concentration reported ranged between 14-820µg/l, which is much higher than prescribed limit by WHO for drinking water. The Task Force revealed that approximately 1.20 lakh people could be affected by arsenic in 55 villages of three blocks (Revati, Dubhad and Belthara Road) of Ballia. Arsenic poisoning in humans causes arsenicosis, The Arsenic Task Force (ATF) has found that the presence of poisonous metalloid in these areas is as high as 50 µg/l. According to WHO (2001) the unsafe level of arsenic in the ground-water is > 10 µg/l.

Mobilization Mechanisms of As

In most studied areas it was seen that high-arsenic groundwater was not related to areas of high arsenic concentration in the source rock. Two key factors were identified:

1. There should be very specific biogeochemical triggers to mobilize arsenic from the solid or sorbed phase to groundwater.
2. The mobilized arsenic should have sufficient time to accumulate and not be flushed away, that is, it should be retained in the aquifer (Smedley and Kinniburgh, 2002). In other words, arsenic released from the source should be quick, relative to the rate of groundwater flushing. There are number of processes for mobilization of arsenic in groundwater namely,
 - (i) Mineral dissolution,
 - (ii) Desorption of arsenic under alkaline and oxidizing conditions,
 - (iii) Desorption and dissolution of arsenic under reducing conditions,
 - (iv) Reduction of oxide mineral surface area, and
 - (v) Reduction in bond strength between arsenic and host mineral surface (Smedley and Kinniburgh, 2002).

Most Common Soil Arsenic Species Most Common Soil Arsenic Species

Arsenic is typically found in the soil in the following forms:

- Organic forms-Arsentate, Arsenite, dimethyl arsenic acid and monomethyl arsenic acid
- Inorganic forms- arsenate, or As (V), and arsenite, or As (III), most common in soil
- Arsenate prevails under aerobic conditions is less toxic and less mobile than arsenite, due to stronger soil sorption.

Health hazards of Arsenic

It is a medical condition that occurs due to elevated levels of arsenic in the body (Naujokas *et al.*, 2013). If exposure occurs over a brief period of time symptoms may include vomiting, abdominal pain, encephalopathy and watery diarrhea that contains blood. Long-term exposure can result in thickening of the skin, darker skin, abdominal pain, diarrhea, heart disease, numbness, and cancer (Ratnaik, 2003). The most common reason for long-term exposure is contaminated drinking water (Naujokas *et al.*, 2013). Groundwater most often becomes contaminated naturally; however, contamination may also occur from mining or agriculture. Recommended levels in water are less than 10–50 ug/l (10–50 parts per billion). Other routes of exposure include toxic waste sites and traditional medicines. Most cases of poisoning are accidental. Arsenic acts via changing the functioning of around 200 enzymes.

Symptoms of arsenic poisoning begin with headaches, confusion, severe diarrhoea, and drowsiness. As the poisoning develops, convulsions and changes in fingernail pigmentation called leukonychia striata (Mees's lines, or Aldrich-Mees's lines) may occur. When the poisoning becomes acute, symptoms may include diarrhea, vomiting, vomiting blood, blood in the urine, cramping muscles, hair loss, stomach pain, and more convulsions. The organs of the body that are usually affected by arsenic poisoning are the lungs, skin, kidneys and liver. The final result of arsenic poisoning is coma and death. Arsenic is related to heart disease (hypertension-related cardiovascular disease), cancer, stroke (cerebrovascular diseases), chronic lower respiratory diseases, and diabetes. Chronic exposure to arsenic related to vitamin A deficiency, which related to heart disease and night blindness (Naujokas *et al.*, 2013).

Current Arsenic Remediation Techniques

1. The problem of Arsenic pollution in ground water in Ballia district has to be immediately addressed too. The first and the foremost task are to identify the villages where Arsenic concentration is above the maximum permissible limit. Arsenic field-testing kit could prove to a very useful instrument to commence the detailed investigations in these areas. The spot analysis of arsenic by field Kit and high concentration of arsenic samples are analyzed Jal Nigam. The hand pumps yielding water with higher Arsenic concentration may be demarcate being paint red etc. These markings would indicate that these pumps are not fit to be use for catering to human or livestock needs.
2. Alternative sources of ground water may be identify and recommended for use. The exploratory wells in different aquifer at different places in arsenic affected area of the district has been constructed by CGWB (**Central Ground Water Board, NR, Lucknow**) to know the arsenic concentration in different aquifer. These exploratory well, which are

free from arsenic, may be utilized by Jal Nigam as production well for drinking water. Now, until date 10 nos of deep tube well (down to 350 m bgl) were constructed by CGWB (Pandey *et al.*, 2009). Arsenic free aquifer is separate from other aquifer by cement sealing within clay layer to check mixing of ground water of different aquifers. Hydro geological tests were conducted at different exploratory well and it was found that no effect was observed on other observation when main well was pumped. It shows that there is no link between different aquifer and cement-sealing technique is properly working.

Alternative remediation- phytoremediation

The removal of a substance from the air, soil, or water via a microorganism or plant is called phytoremediation. Phytoremediation of arsenic-contaminated groundwater is a relatively new idea (Tu and Ma, 2002; Tu *et al.*, 2004). Phytoremediation takes advantage of the unique, selective and naturally occurring uptake capabilities of plant root systems, together with the translocation, bioaccumulation and pollutant storage/degradation abilities of the entire plant body. A wide range of plant species has been identified as being arsenic resistant. Many researchers reported that ferns can highly absorb toxic and carcinogenic substances, heavy metals, from contaminated soils, that opened up the possibility for its use for remediation of soils. Successful application of phytoremediation to arsenic contaminated soils depends on many factors, among which plant biomass and arsenic concentration are the most important. Plant species used to extract arsenic should be responsive to agricultural practices designed to enhance arsenic accumulation and to allow repeated planting and harvesting of arsenic-rich biomass (Tu and Ma, 2002). In India, *Pteris Vittata* L. is very common and widely distributed. It is found on almost any calcareous substrate, such as old masonry, sidewalks, building crevices, with exposed limestone, among the known arsenic hyperaccumulators, *P. vittata* (brake fern) is one of the most efficient and most studied plants. Brake fern effects, reported that the *P. vittata* is extremely efficient in extracting arsenic from soils (Ma *et al.*, 2001). Vetiver grass possesses the ability to grow well in every soil arsenic concentration. It is recommended that Vetiver grass could be used to remove arsenic contaminated soil (Hosamane, 2012).

Several subdivisions of phytoremediation are phytovolatilization, phytoextraction, phytostabilization, and rhizofiltration. This technique for arsenic removal is

- Low Cost
- Environmentally –friendly
- Much lower occupational risk

Arsenic is a chemical analog to phosphorus (i.e. it is easily taken up by plants)

Properties of Arsenic Accumulating Plants - hyperaccumulators

- Plant accumulates greater than 1000 mg of contaminant per kg DW
- Bio -concentration Factor (BF) > 1 , ratio of plant to soil arsenic concentration
- Translocation Factor (TF) > 1 , ratio of aboveground biomass to root system arsenic concentration f

Accumulation concentration of a contaminant greater than 100 times than the highest value for a non - hyperaccumulating plant

Examples–*Pteris* ferns, *Pityrogramma calomelanos*, *Lemna gibba* (duckweed), *Lepidium sativum* (watercress), *Lupinus albus* (white lupin), Mustard Plants (Hemen, 2011)

Why use a hyperaccumulator?

- Decrease amount of time needed to remediate contaminated area
- Reduce volume of contaminated biomass
- Makes phytoremediation a realistic option

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Received on 14.02.2016 and accepted on 22.05.2016