

### Chapter-3

## **Sources and Causes of Groundwater Arsenic Contamination in Ganga-Brahmaputra Plains**

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Arsenic (As) in groundwater has been reported, mostly in areas formed by recent alluvial sediments, describing Holocene aquifers (< 12 thousand years of age) of the Ganga-Brahmaputra Plains, where the concentration is exceeding from acceptable level, that is, 50 µg/L. Almost all the identified arsenic affected areas, in the Gangetic plains, are in a linear track on either side of the River Ganga in UP, Bihar, and Jharkhand, or the River Bhagirathi in West Bengal, except areas in Chhattisgarh and 3 districts of Bihar namely, Darbhanga, Purnea and Kishanganj. The areas in Assam and Manipur are in the flood plains of the Brahmaputra and Barack, respectively. Ironically, all the arsenic affected river plains have the river routes originated from the Himalayan region. Whether the source material has any bearing on the outcrops or not 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.

Though the exact geochemical processes are yet to be established, arsenic in groundwater in the Holocene aquifer is believed to be released from soil, under conditions, conducive to dissolution of arsenic from solid phase on soil grains to liquid phase in water. The constituents and environmental conditions of the soils have, thus, a greater influence on arsenic speciation and mobility than the total concentration in soils. The occurrence of As in soils and aquifer formations is, thus, a subject matter of greater interest.

### **3.1 Probable Natural Sources**

There is no proof regarding the natural emission of As in the Ganga-Brahmaputra plains so far. 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. Arsenic concentration (NAS, 1977; Crecelius and Bothner, 1975) in different sediments could be as high as 490 mg/kg. 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; BGS/MML, 1999). The source of groundwater arsenic contamination, in the Ganga-Brahmaputra basin, is yet to be established. Weathering of As-rich sulphides, such as pyrite, releases bivalent Fe, which readily forms amorphous oxyhydroxides in an oxidizing environment that would strongly sorb co-weathered arsenic (Mok and

Wai, 1994; Thornton, 1996). Groundwater of the reducing sedimentary aquifers is characterized by high concentrations of dissolved iron due to the reductive dissolution of iron oxy-hydroxides that mobilize the sorbed arsenic. Studies on the hydro-geochemistry of the BDP groundwater (Chakraborti et al., 2003; Acharyya, et al., 1999; Bhattacharya et al., 2002) have revealed elevated concentrations of Fe (145-8624  $\mu\text{g/l}$ ) in groundwater, whereas iron concentration in groundwater in Bihar ranges from below detection limit to 700  $\mu\text{g/L}$ . Irrespective of the concentration of Fe in groundwater, the process for its release is triggered by the reduction of Fe oxy hydroxides in the Ganges sediments, with consequent release of arsenic.

As concentrations in groundwater of the Bengal Basin vary widely, it generally ranges from less than 5  $\mu\text{g/L}$  to 3200  $\mu\text{g/L}$  (CGWB, 1999; BGS and DPHE, 2001). But in certain areas, concentration up to 4100  $\mu\text{g/L}$ , has been identified (Ghosh and Mukherjee, 2002). 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 Jamuna in the northeast (Acharyya et al., 2000).

There has been much speculation about the primary source of arsenic in the Bengal basin. The total amount of solid-phase arsenic, which ranges from 1 to 30 mg/kg, in the soil and sediment, is not significant (McArthur et al., 2001; Harvey, 2002). Several investigators have reported that the contamination is natural and is intensified by anthropogenic interferences (Acharyya et al., 1999, 2000; Ray, 1999). The hypotheses about the sources of arsenic in the BDP are as follows:

- (i) 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).
- (ii) 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).
- (iii) Arsenic is transported with the fluvial sediments from the Himalayas (e.g., McArthur et al., 2004). This is the most accepted hypothesis at present.

### **3.2 Anthropogenic Sources**

The release of arsenic from different sources is often cited in the literature (Boyle and Jonasson, 1973; Berdowski et al., 1997), but there is still lack of information on atmospheric emission of arsenic in eastern regions of the Indian subcontinent. Average concentration of arsenic in Indian coal ranges up to 3.72 mg/kg, with a maximum value of 40 mg/kg (e.g. Sohagpur coalfield, Northeastern India) (Khandekar et al., 1999; Warwick et al., 2001). Hence, it is believed that coal combustion in Eastern India is one of the major sources of anthropogenic

arsenic emission in the environment. There are several metallurgical plants, cement factories, incineration and chemical industries in eastern and Northeast India which contribute to the emission of arsenic into the environment. However, there is no data available, on the exact tonnage of arsenic entering the environment. A secondary leading industry near greater Kolkata, West Bengal, releases arsenic to the environment. The maximum concentration in soil of that area was reported to be  $9740 \pm 226$  mg/kg while the minimum was  $17.5 \pm 0.52$  mg/kg (Chatterjee and Banerjee, 1999). Leaching of arsenic in groundwater is also expected in the vicinity of areas of landfills containing waste and hazardous waste piles (Boyle and Jonasson, 1973; Tripathi et al., 1997; Pandey et al., 1998). The use of fertilizers and insecticides also causes high concentration of arsenic in soil compartments. There is a lack of information on the anthropogenic deposition of arsenic, within the extensive alluvial tract of the Ganga-Brahmaputra river basin. The arsenic-affected areas are the parts of the lower delta plain of the Ganges and foothills of Brahmaputra and Barak valley. 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. However, it has been contemplated that the Ganges-Brahmaputra basin has rather been undisturbed by anthropogenic sources compared to industrialized countries, where river basins have generally been affected by industrial activities (Huang et al., 1992).

### **3.3 Occurrences of Arsenic in Groundwater**

Several studies suggested that the groundwater arsenic contamination is mostly restricted to the alluvial aquifers of the Ganges delta comprising sediments carried from the sulphide-rich mineralized areas of Bihar and elsewhere surrounding the basin of deposition (Bhattacharya et al., 1997; Das et al., 1995). However, recent studies indicated that the vast tract of Indo-Gangetic alluvium extending further to the west and the Brahmaputra alluvium have elevated concentrations of arsenic in wells placed in the late Quaternary and Holocene aquifers. *Arsenic released during the weathering of sulphide minerals is generally adsorbed onto the surface of iron oxy-hydroxides that precipitated under oxidizing conditions normally prevailing during the deposition of the Holocene sediments. However, redox processes in the sediments triggered the reductive dissolution of iron oxides that transferred substantial amounts of arsenic in aqueous phases through biogeochemical interactions (Amaya, 2002; Smedley and Kinniburgh, 2002).* Arsenic-containing groundwater in Ganga-Brahmaputra River basin is hosted by the sediments deposited by the rivers during the late Quaternary or Holocene age (< 12 thousand years). Lithology of those late Quaternary sediments includes sands, silt and clay. Mineralogical composition of those sediments consists of quartz, feldspars, illite and kaolinite and the fine-grained over bank facies are rich in organic matter (Nickson et al., 1998; Ahmed, 1999; Datta and Subramanian, 1998; Sikdar and Banerjee 2003). There is a thick layer of newer alluvium containing sand, silt and clay, which spread out by numerous rivers that originate from the Himalayas both in the north and northeast. *Most environmental arsenic problems, recognized so far, are the result of mobilization under natural conditions.*

### 3.4 Mechanisms of As Mobilization

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: first, there should be very specific biogeochemical triggers to mobilize arsenic from the solid/sorbed phase to groundwater, and second, 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 holt mineral surface (after Smedley and Kinniburgh, 2002).

*Oxidation of sulphide minerals (pyrite-FeS<sub>2</sub>) was advocated strongly by many investigators in West Bengal as the cause of groundwater arsenic contamination (Das et al., 1994). According to this hypothesis, arsenic is released from the sulfide minerals (arseno-pyrite) in the shallow aquifer due to oxidation (Mandal et al., 1998). The lowering of water table owing to over exploitation of groundwater for irrigation is the cause of release of arsenic.* The process can be explained as: the large-scale withdrawal of groundwater causes rapid diffusion of oxygen within the pore spaces of sediments and, thereby, increases dissolved oxygen in the upper part of groundwater. The newly introduced oxygen oxidizes the arseno-pyrite and forms hydrated iron arsenate compound known as pitticite in presence of water. This compound being very soft and water-soluble, the light pressure of tube-well water breaks the pitticite layer into fine particles and make it readily soluble in water. It then seeps like drops of tea from the teabag and percolates from the subsoil into the water table. When the tube-well is in operation, it comes out with the extracted water (Safiuddin and Karim, 2001). Such oxidation processes could explain possible mechanism of As mobilization in some parts of the aquifers, particularly at the shallowest levels but may not be the main cause of groundwater arsenic contamination in the Ganges-Brahmaputra river basin. *A recent research study explained that desorption or dissolution of arsenic from iron oxides could be the process on regional distributions of arsenic in water (Smedley, 2004).* According to this process, a series of changes in the water and sediment chemistry as well as in the structure of iron oxides take place at the onset of reducing conditions in aquifers. Many of these changes are poorly understood on a molecular scale. *Broadly, it can be stated that some critical reactions to transform to reducing conditions and subsequent arsenic release are likely to take place to reduce arsenic from its oxidized (As(V)) form to its reduced (As(III)) form.* Under many conditions, As (III) is less strongly adsorbed to iron oxides than As (V); and reduction in such case involves a net release from adsorption sites. *Dissolution of the iron oxides themselves under reducing conditions is another potentially important process.* Under aerobic and acidic to neutral conditions, adsorption of arsenic (As (V)) to iron oxides is normally strong and aqueous concentrations are usually low. However, the sorption is less strong at high pH.

Increases in pH (especially above pH 8.5 or so) will, therefore, result in desorption of arsenic from oxide surfaces that, in turn, will increase arsenic in dissolved concentrations. Such processes are considered responsible for the release of arsenic in oxidizing Quaternary sedimentary aquifers. In addition, the role of microorganisms in the leaching of arsenic from sediments can not be over ruled. In this process, arsenic mobilization occurs by microbial degradation in the presence of organic substrates in reducing aquifers (Bhattacharya et al., 1997; Bhattacharya et al., 2001). Burial of organic matter along with the sediments facilitates microbial activity, which plays an important role in the generation of reducing conditions (BGS and DPHE, 2001; McArthur et al., 2001). The rates of arsenic release under such conditions depend on a number of factors, including rates of sedimentation, diffusion of gases and microbial reactions, but could be relatively rapid on a geological timescale. The onset of reducing conditions and release from iron oxides is believed to be the main process controlling high arsenic concentrations in sedimentary aquifers. The nature of the organic matter involved in the generation of reducing conditions in arsenic- affected aquifers has been disputed in recent years (BGS and DPHE, 2001; McArthur et al., 2001; Harvey et al., 2002). The shallow groundwater system in the Bengal delta plain is more complicated due to the presence of organic matter, which governs the biogeochemical processes of arsenic mobilization (McArthur et al., 2001). Whatever be the nature of the organic matter present, its importance in controlling the redox conditions in reducing aquifers such as those of the Bengal basin is widely acknowledged. The surface reactivity of iron (Fe) and aluminum (Al) plays an important role in adsorbing the bulk of arsenic in the sedimentary aquifers in the Ganges-Brahmaputra basin. *However, the theory lacks in explaining increasing arsenic concentration in existing tube-wells, which were previously safe but progressively contaminated over time (Roy Chowdhury et al., 1999). Sediment analyses showed that extensive groundwater withdrawal for agricultural purposes favored the oxidation of arsenic-rich iron sulphide and thereby mobilization of arsenic in the Bengal Basin (Nickson et al., 2000; Das et al., 1996; Roychowdhury et al., 1999).* Adsorption to hydrous aluminum and manganese oxides may also be important, in case they are present in significant quantity (Peterson and Carpenter, 1983; Brannon and Patrick, 1987). It was speculated that phosphate concentrations in groundwater of the BDP resulted from application of fertilizers (Acharyya et al., 1993; Acharyya et al., 1999; Sikdar 2003). But it seems to be unconvincing because the amount of dissolved and sorbed phosphate in the aquifer volume is found exceeding the amount of phosphate applied as fertilizer (Bhattacharya et al., 2002). *Excessive use of water for irrigation and use of fertilizers have caused mobilization of phosphate from fertilizers down below the shallow aquifers, which have resulted in the mobilization of As due to anion exchange onto the reactive mineral surfaces.* Since phosphate is bound strongly onto these surfaces,  $As^{5+}$  can be mobilized in groundwater (Acharyya et al., 1993). It is also observed that phosphorus in groundwater cannot contribute to arsenic pollution (Manning and Goldberg, 1997).

Sikdar and Banerjee, (2003) attributed cause of arsenic to the extensive use of lead arsenate and copper arsenite as rhodenticides and pesticides rather than geological or

*geo-morphological settings*. The redox balance tilted towards a reducing environment, due to the organic rich argillaceous sediments deposited in fluvio-deltaic marshes and triggered by recent heavy groundwater abstraction and use of phosphate fertilizers.

XRD analysis revealed that illite was the dominant clay mineral in the clay/silty clay partings. No arsenic bearing mineral phase was identified in the clay or in the sands in the arsenious zone. The concentration of arsenic in sediments generally decreased with depth. And arsenic showed high positive correlation with iron, manganese, copper and lead and low correlation with zinc based on multiple correlation analysis. These observations were related with extensive use of lead arsenate and copper arsenite as rhodenticides and pesticides in jute cultivation.

A study carried out by Sikdar and Chakraborty (2008) in the western part of the alluvium-filled gap between the Rajmahal hills on the west and the Garo hills on the east to understand the importance of hydro-geochemical processes involved in the groundwater evolution, with special emphasis on the genesis of arsenic in the aquifer system using statistical methods, indicated that *the combined processes of recharge of groundwater from rainfall, sediment water interaction, groundwater flow, infiltration of irrigation return water (which is arsenic rich due to the use of arsenic-bearing pesticides, wood preservatives, etc. and the pumping of arsenic-rich groundwater for agriculture purpose), oxidation of natural oranthropogenic organic matter and the reductive dissolution of ferric iron and manganese oxides, played a key role in the evolution of groundwater arsenic contamination in the area*. From another PCA (Principal component analysis) with geologic, geomorphic, anthropogenic, geochemical and land-use factors indicated that arsenic concentration in groundwater increased with increasing area of mango orchards, sand lithofacies and nitrate. The organic carbon, available from decomposition of waste material undergone oxidative carbon degeneration by different oxidants, increased the concentration of CO<sub>2</sub> in the aquifer. The reducing condition, thus, developed in the aquifer helped dissolve the arsenic adsorbed on iron hydroxide or oxy-hydroxide coated margins of sand, iron rich heavy mineral grain margins, clay minerals and Fe-Mn concretions present in the aquifer matrix.

*Recently, a new hypothesis based on displacement of arsenic by dissolved bicarbonate as an alternative mechanism for the genesis of high-arsenic groundwater has been proposed (Smedley and Kinniburgh, 2002). It seems that there are number of hypotheses, which have their own discrepancies and limitations to explain the physical processes*. Therefore, a need arises for integrated research in order to understand sources, release mechanisms, and mobilization of arsenic in sedimentary aquifers.

The natural As-pollution in Bangladesh has been reported to be from reductive dissolution of sedimentary iron oxide (FeOOH) (Nickson et al. 1998), which strongly sorbs arsenic, although details of the process continue to emerge (e.g. Tufano and Fendorf, 2008). What controls the distribution of arsenic-pollution in an aquifer is less clear, but of greater

importance for aquifer development, health, and remediation. Early work (DPHE, 1999) showed that sea-level change strongly influenced the distribution of arsenic-pollution, apparently confining it to sands deposited after the low-stand of sea-level at the Last Glacial Maximum (LGM;  $\approx 20$  ka; Umitsu 1993, Lambeck et al. 2002); wells screened in underlying older sands were believed in 1999 to be arsenic-free. But of wells in the post-LGM aquifers, only 50% are polluted by arsenic above the concentration level of  $50 \mu\text{g/L}$ , and a full 75% contained less than the local drinking-water limit of  $50 \mu\text{g/L}$ , so sea-level variations alone could not explain the distribution of arsenic-pollution.

Polizzotto et al., (2008) using hydrologic and (bio)geochemical measurements, showed that on the minimally disturbed Mekong delta of Cambodia, arsenic is released from near-surface, river-derived sediments and transported, on a centennial timescale, through the underlying aquifer back to the river. Owing to similarities in geologic deposition, aquifer source rock and regional hydrologic gradients their results represented a model for understanding pre-disturbance conditions for other major deltas in Asia. Furthermore, the observation of strong hydrologic influence on arsenic behavior indicated that release and transport of arsenic are sensitive to continuing and impending anthropogenic disturbances. In particular, groundwater pumping for irrigation, changes in agricultural practices, sediment excavation, levee construction and upstream dam installations will alter the hydraulic regime and/or arsenic source material and, by extension, influence groundwater arsenic concentrations and the future of this health problem. This model was supported by Harvey (2008) who postulated that the arsenic originally came from eroded Himalayan sediments, had been washed down into low-lying regions. It is widely believed that this arsenic dissolves and enters the groundwater under anaerobic conditions. It is, therefore, unsurprising to find that highly contaminated groundwater originates from pond sediments: the steady settling and decomposition of organic material at the bottom of tropical ponds take up all the oxygen that diffuses, or is carried by downward flow, into the sediment. Water passing through pond sediments could also contain organic carbon that, on decomposition, might help liberate arsenic from deeper sediments, adding to the contamination. But any organic carbon that is already contained in deeper aquifer sediments probably contributes less to biogeochemical processes because it is not replenished, and what remains is typically of low reactivity.

The model proposed by Polizzotto and Harvey was contradicted by Sengupta et al., (2008) from their analysis of time-series data collected over two years for  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , and Ca, Mg, K, and Cl, concentrations for 10 ponds in, and upflow of, an arsenic-polluted region of southern West Bengal. They compared the compositions of As-polluted groundwater from wells with the compositions of waters in ponds upflow and within the range of influence of the wells; and revealed that conservative tracers ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , K), and other tracers (Ca, Mg) of pond-water and groundwater were distinct and there were no overlaps between the composition of two sources. These indicated that water from ponds was not the source of arsenic in the contaminated groundwater.

### **3.5 Transport modeling to understand arsenic movement**

Geochemical, physicochemical and biological characteristics usually explain chemistry of arsenic with regard to its occurrence, release, dissolution, sorption, mechanism, etc. in soil-water phases at local scale. Groundwater, being dynamic, when it is in a specific hydro geologic setup, fate assessment of point values of arsenic concentration in terms of distribution and transport in a groundwater domain on a regional scale could provide a good insight to understand movement of arsenic in that domain. Numerical groundwater flow and transport modeling is one of the powerful techniques by which one can determine spatial and temporal distribution of arsenic mobilization, understanding of transport phenomena, zoning of fresh and contaminated water, etc. that can help evolve management strategies of an aquifer for different stress conditions under a framework of hydro-geological setting. Modeling is a framework of computational tool, basically derived from the conceptualization of processes, which are otherwise known, but modeling itself cannot explain the physical processes. Numerous studies have been attempted by many investigators related to modeling of groundwater arsenic contamination, however, the findings of numerical modeling has remained mere exercises with number of 'ifs and buts' owing to lack of proper understanding of chemistry of arsenic in the geo-environmental and geochemical processes.

National Institute of Hydrology (NIH) and CGWB in year 2001 carried out a modeling study in the Yamuna sub-basin, Nadia, and North 24-Paraganas districts to quantify spatial and temporal variation of arsenic contaminated groundwater for different geo-hydrologic settings and to suggest possible remedial measures for the arrest of spreading. It was reported from the study that the distributions of observed arsenic concentration have local high peaks with spreading in their surroundings implying localized in-situ sources spread over in the vicinity of the source by the influence of groundwater movement exaggerated by exploitation. And their localized activation has no bearing on the influence of sources from other domain or by the mobilization of arsenic from one pocket to another: those had been propagated by the local disturbances. From another analysis, it was shown (Majumdar et al., 2002 ) that by appropriately locating pumping wells in the freshwater zone, within the scattered zones of arsenic contaminated water, one can withdraw arsenic free groundwater without influencing movement of arsenic in the contaminated zones. In other words, it indicated that by adopting appropriate aquifer management strategies, fresh groundwater tapping from the scattered zones of fresh water, adjoining to the zones of arsenic contaminated water is possible without perturbing movement of arsenic from the contaminated zones.

Michael and Voss (2008) derived a method for reducing the concentration of arsenic in the Bengal Basin's water supply, from a groundwater modeling study, which could provide the population with safer water for drinking and irrigation. As an alternate to other solutions such as ex-situ treatment of arsenic contaminated water by filters, the authors performed a quantitative, large-scale hydro geologic analysis and numerical simulation of the entire Bengal Basin, looking



at the benefits of water wells that pump from depths where the water is less contaminated. The authors showed that by installing wells to depths >150 m and using that water only for households could provide 90% of the region with low-arsenic water for 1,000 years. Water for irrigation would continue to be taken from near the surface because using the deep aquifers for both purposes could stress the resource, potentially drawing surface arsenic into the deeper reservoirs. Simulations provided two explanations: deep domestic pumping would slightly perturb the deep groundwater flow system, while substantial shallow pumping for irrigation would form a hydraulic barrier for protecting deeper resources from shallow arsenic sources. The analysis, further, indicated that this simple management approach could provide arsenic-free drinking water to >90% of the arsenic-impacted region for a period over 1,000-year.

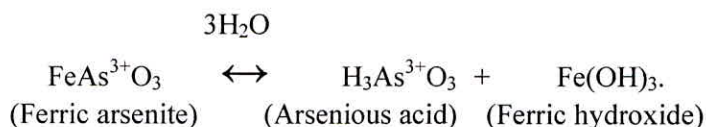
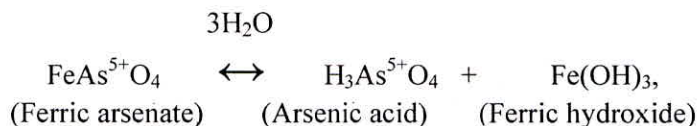
Paul and Sikdar (2008) carried out numerical modeling of groundwater arsenic contamination movement for the English Bazar Block, Malda District, West Bengal. The study indicated that high abstraction of groundwater because of irrigation requirement has led to both horizontal and downward vertical movement of arsenious water within the aquifer towards the fresh water zones. The pattern of path-lines of groundwater flow was delineated quite different from the pre-development case. It was recommended from the above studies that if the abstraction rate is increased to 100m<sup>3</sup>/hr then within 50 years, there is a possibility of the aquifer getting contaminated but if the rate is decreased to 30m<sup>3</sup>/hr then the aquifer may remain uncontaminated at least for the next 50 years.

There are several other groundwater arsenic modeling studies. The points primarily advocated in most of the modeling studies are: (i) sources of arsenic in groundwater system are in-situ and in localized patches, and their mobilization is governed by exploitation of the groundwater regime, (ii) by adopting judicious aquifer management, arsenic free groundwater can be tapped for a long period with no risk of perturbing arsenic contaminated zones, and (iii) tapping of deep uncontaminated aquifer and freshwater zones in conjunction with surface water source may ensure supply of arsenic free water both for drinking and agricultural requirement.

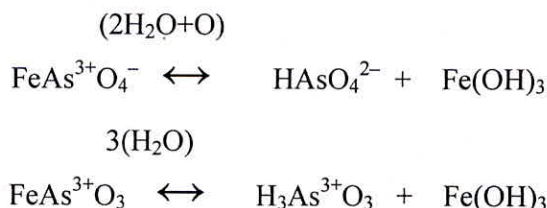
### **3.6 Chemical processes of arsenic contamination**

Although there are number of hypotheses explaining chemical processes groundwater arsenic contamination, however, the most commonly believed chemical processes are dissolution.

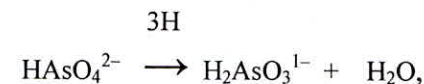
Iron arsenate (FeAsO<sub>4</sub>) may be tentatively regarded as the direct and immediate source of arsenic, because it is easily formed from scorolite [FeAs<sub>4</sub>, 2H<sub>2</sub>O] and pitticite (hydrated mixture of arsenate and sulphate), that are common alternation products of arsenopyrite. Since arsenopyrite can contain As (III) ions in small proportion with ions of As (V), which is the dominant constituent, it is quite likely that arsenic in the alluvium occurs as ferric arsenate (FeAsO<sub>4</sub>), with ferric arsenite (FeAsO<sub>3</sub>) in minor proportion. Due to hydrolysis under conditions of low pH and high Eh, ferric arsenate is dissociated into the strongly poisonous arsenic acid (H<sub>3</sub>AsO<sub>4</sub>)



Ferric hydroxide is soluble in acidic aqueous environment, but it is precipitated in alkaline and reducing conditions at low Eh. Thus, if the acidity of the solution decreases (pH increases), colloidal precipitation of ferric hydroxide takes place. Some As (V) and As (III) ions being absorbed on the particles of Fe (OH)<sub>3</sub>, may be co-precipitated with the latter. This reduces arsenic content of water. However, precipitation of As (V) and As (III) is not simultaneous because As (III) is 5 to 10 times more soluble than As (V) and its stability in aqueous solution increases with the alkalinity of water and reducing character of the environment. Thus, even after colloidal precipitation of As (V) ions with ferric hydroxide, the aqueous solution may contain As (III) ions in large amount. In mildly acid to neutral solution (pH ≤ 7) or even in mildly alkaline solution under oxygenated condition at Eh > 0, breakdown of ferric arsenate and ferric arsenite by hydrolysis can produce As (V) bearing arsenic acid (HAsO<sub>4</sub><sup>-2</sup>) and As(III) bearing arsenious acid (H<sub>3</sub>AsO<sub>3</sub>) respectively, together with ferric hydroxide in both cases. The relevant equations are:



Arsenous acid (HAs<sup>5+</sup>O<sub>4</sub><sup>2-</sup>) is the commonest of arsenate compounds in natural water as aqueous solution. In a mildly reducing environment, HAsO<sub>4</sub><sup>2-</sup> is converted into As (III)-bearing arsenious acid (H<sub>2</sub>AsO<sub>3</sub><sup>1-</sup>) and in a strongly reducing condition into arsenious acid (H<sub>3</sub>AsO<sub>3</sub>). The change can be shown by the following equations:



In the absence of As (III) in the source material (FeAsO<sub>4</sub>), As(V)-bearing arsenic acid (HAsO<sub>4</sub><sup>2-</sup>) can be formed by the hydrolysis of FeAsO<sub>4</sub> in a mildly alkaline and oxygenated environment and ferric hydroxide is produced at the same time.

In the biomethylation process, arsenic in the sediment is hydrolysed to arseneous acid and is further reduced by bacteria to  $\text{As}^{3+}\text{O}(\text{OH})$  that form arsenite in solid state. Thus, the first role of bacteria is to increase the ratio of As (III)/As (V) in the sediment. This As (III) readily goes into aqueous solution to increase arsenic toxicity of water. The next step of change brought about by bacteria is biomethylation of  $\text{As}^{3+}\text{O}(\text{OH})$ , resulting in the formation of  $\text{CH}_3\text{As}^{3+}\text{O}(\text{OH})_2$  or methyl arsenic acid and  $(\text{CH}_3)_2\text{As}^{5+}\text{O}(\text{OH})$ , i.e. dimethyl arsenic acid or cacodylic acid, which is an extremely toxic compound. In each step, these substances are soluble in water to increase toxicity. In the fourth step, cacodylic acid is again biomethylated to form  $(\text{CH}_3)_3\text{As}^{3+}$  or trimethylarsine by aerobic bacteria under oxidizing condition, whereas, anaerobic bacteria under reducing condition convert cacodylic acid to  $(\text{CH}_3)_2\text{HAS}^{3+}$  or dimethyl arsine. Both are soluble in water and are toxic. The biomethylation process increases the proportion of organo-arsenic, which is readily absorbed by plants and animals through soil and water. Thus, the arsenic content of soil and water is reduced. However, the unabsorbed part of the organo-arsenic being toxic pollutes the soil and water. Hence, the practice of drawing arsenic contaminated groundwater from tube wells for irrigation purposes may ultimately lead to poisoning of surface soil and surface water, which are normally arsenic-free even in arseniferous regions of West Bengal.

The Brahmaputra alluvial basin is bounded by lower Himalayan Mountains in the north and northeast. High intensity of rainfall in the catchments and plain areas has contributed to high sediment loads, which have developed the valley into a long stretch of recent and old alluvium. The alluvium near the river is sandier and periodic fluvial action keeps the alluvium stratified. However, its influence has been gradually obliterated by climate as one move from recent flood plains to old flood plains and then upland. As a result, there is deposition of coarse sand and coarser river-borne materials along with plant cells and other organic materials cells which may contain considerable amount of arsenic and other toxic elements. During the course of time, arsenic elements get released in the reducing environment by the process of biomethylation and get shelter within silty and clayey sediments. Some studies (Bhattacharya et al., 1997; Nickson et al., 1998 and others) also put forward the hypothesis that the burial of sediments, rich in organic matter, led to strongly reducing conditions in groundwater aquifer, which is facilitated by high water table, fine grained surface layers and widely practiced wetland paddy cultivation, as well as microbial oxidation of sedimentary organic matter, depleting, thereby, the dissolved oxygen in groundwater. Arsenic is released when arsenic rich iron oxyhydroxides, which are efficient arsenic scavengers, are reduced in anoxic groundwater. Such reduction is driven by concentrations of sedimentary organic matter.

*Many experts agreed that the source of such high arsenic, anomaly in groundwater is geological rather than from pesticides or other artificial sources. It is postulated that arsenic bearing sulphide minerals, the commonest of which in nature is arsenopyrite ( $\text{FeAsS}$ ) and/or its alternation products, had been transported in the geologic past possibly from those occurring along the foothills of the Himalayas and deposited with the alluvium in*

*the Ganges-Brahmaputra basin. These extraneous arsenic minerals buried under the recent alluvium are considered to be responsible for contamination. However, arsenopyrite and its alternation products are less toxic and normally insoluble in water. Over and above this, high arsenic anomaly has suddenly appeared in recent times, as no report of arsenic contamination of groundwater can be traced earlier than the late seventies. In the present condition of emergence of greater area with arsenic pollution, the relation between chemistry of arsenic and high arsenic anomaly in groundwater is an interesting subject of study.*

### **3.7 Observations, Analysis and Appraisal**

Arsenic contaminations in groundwater have affected highly fertile and thickly populated Bengal Delta, Middle Ganga Plain, parts of Brahmaputra Plain and some alluvial areas of North-Eastern Regions. It is by and large influenced by common geomorphological setting and sedimentation pattern associated with Pleistocene-Holocene sea level changes. Shallow level arsenic contaminated aquifers of Holocene age are extensive over low-lying Bengal Delta and discontinuously along narrow entrenched channels in the Middle Ganga Plain. The oxidised Pleistocene sediments are generally free from arsenic. The Late Pleistocene and associated oxidized sediments constituted the interfluvial areas of organic rich Holocene flood plain and deltaic sediments in the Bengal Delta and Middle Ganga Plain and the Barind. The presence of Late Pleistocene palaeosol aquitard apparently protects the underlying sediments from the downward movement of arsenic bearing and organic rich groundwater which might cause arsenic contamination. The arsenic contaminated aquifers in the Terai belt, Nepal, are closely comparable in nature and age to that of the Bengal Delta. The sediments in the Middle Ganga Plain and in the Bengal Delta are mainly derived from the Himalaya with minor contribution from the Peninsular India. In the Dongargarh Proterozoic rift-zone, in Chhattisgarh, arsenic concentration was enriched in acid magmatic rocks. In some of its local areas, arsenic and iron were enriched further in weathered rocks and soils, where Arsenic is adsorbed on hydrated-iron-oxide (HFO), which occurs as coating on clay minerals, biotite, and chlorite. In the Bhagirathi-Ganga Delta, Middle Ganga Plain and other arsenic-affected alluvial basins, Arsenic bearing pyrite or any other arsenic minerals are virtually absent in their aquifer sediments. Arsenic generally occurs as adsorbed on HFO, which preferentially enriched fine grained, fluvial and deltaic sediments and occur as coatings on quartz, clay, ferromagnesian clastic grains and organic matter.

Among few hypotheses proposed to explain the possible mechanism of arsenic groundwater contamination, most scientists have settled down to two hypotheses: (i) oxidation of arsenopyrite or arsenic rich pyrite in soil strata, and (ii) reductive dissolution of arsenic from soils.

The oxidation hypothesis considers that due to heavy withdrawal of groundwater, aquifer was aerated and oxygen entering into the aquifer oxidised the pyrites rich in arsenic and acid released in the oxidation process leached the arsenic in soluble form in groundwater. While

some scientists believe that the reductive desorption and dissolution of arsenic adsorbed onto iron oxyhydroxides in recent sediments is the most probable mechanism of arsenic mobilization in groundwater.

The oxidation hypotheses lack the merit as no arsenopyrite or pyrite rich in arsenic could be detected in widespread areas. Very low concentration of sulphate in groundwater is also contrary to pyrite oxidation hypothesis. On the other hand, the reduction hypothesis is getting considerable support from various studies. The soils in deeply submerged areas promote growth of aquatic weeds and increased agricultural wastes, most of which are mixed up with soil and buried underground and finally decay anaerobically. The anaerobic process provides a reducing environment of low redox condition for dissolution of iron and arsenic from solid phase to the liquid phase in groundwater.

Microbial arsenic reduction is also emerging as a potentially important factor in aquatic arsenic mobility. Bacterial action e.g. *Thiobacillus Ferroxidans* can assist the oxidation of  $Fe^{2+}$  (aq) in the presence of dissolved oxygen. Investigations have revealed microbial transformations of As (V), a form that adsorbs strongly to sediment solids to As (III), a form that is often much more mobile. As this process generates energy for the microbes involved, it has the potential to modify arsenic speciation of a system both rapidly and extensively.

Some scientists argued that arsenic contamination has been created by imprudent human interventions on nature. The modern system of agriculture has introduced an environment in which huge amount of fertilizers, pesticides, agrochemicals and groundwater for irrigation caused physical interventions changing the natural flow of irrigation setting of the country.

From the available information and results of various research works, it is considered that a combination of oxidation and reduction phenomena coupled with changes introduced by organic matter present in the sediments might have contributed largely for such high mobilization of arsenic. Large scale groundwater withdrawal during summer months causes lowering of Water table and enhances oxidized zone. During monsoon months the sediments are subjected to reducing environments with large quantities of rainfall recharge. As redox conditions become increasingly reducing, the ferric iron is reduced to, resulting in mobilization of some of the adsorbed arsenic. The Wetland cultivation with increased microbial activity further aggravates the problem.

Ground water in Bengal Deltaic Plain is anoxic in nature and mostly Calcium bicarbonate type in which sedimentary iron [both Fe (II) and Fe (III)] deposited by the meandering river carries arsenic. Sediment mineralogy and texture along with organic matter play crucial role in release of As in groundwater. High redox sensitive species (As, Fe and Mn), high alkalinity and absence of dissolved oxygen and nitrates suggest the microbial mediated and thermodynamically

favoured redox processes (denitrification→ iron reduction). The presence of amorphous Fe-oxide together with surface bound phosphate in hotspot areas, and Fe-oxides as well as carbonate and phosphate minerals are also playing significant role in arsenic mobilization. It has been observed that As (III) is more dominant in near-surface aquifers rich in organic matter.

Release of arsenic to groundwater is mainly caused by reductive dissolution of hydrated iron oxide (HFO) and corresponding oxidation of organic matter. Groundwater flow, particularly during recharge of aquifers brings dissolved organic matter, in contact with HFO, promoting its bio-mediated reductive dissolution and consequent release of iron and arsenic to groundwater. High concentrations of arsenic are common in alluvial aquifers of the Bengal Basin and Mid Ganga Plain and arise because erosion of Himalayan region supplies immature sediments with low sulphate loadings of FeOOH on mineral grains, to a depositional environment that is rich in organic matter so that complete reduction of FeOOH is common. The role of human interventions, in increasing recharge of groundwater consequent to groundwater withdrawal during pre-monsoon period and enhancing the process of reduction, may also be quite significant.

Although level of information in Lower Ganga Plain is quite substantial, research work on mobilization of arsenic in Mid Ganga Plain and Brahmaputra Plain has to be geared up to arrive at a more precise understanding on the processes involved.

### **3.8 Summary**

Findings of many research studies are yet to explain precisely actual causes, sources and mechanisms in a boarder perspective. The studies have mostly remained in search of causes, mechanisms and in identification of 'pros and cons' at micro-level. Groundwater flow and contaminant transport modeling studies could settle down suggesting different options of aquifer management to provide arsenic free groundwater from a contaminated aquifer without influencing much mobilization of arsenic contaminated water. Efforts for in-situ remediation of arsenic contaminated aquifer have already been initiated in West Bengal. It is strongly believed that there is a need for integrated research to identify genesis of arsenic and its mechanism of release and mobilization in the soil-water system. There is also a need for developing methods for in-situ remediation and groundwater management strategies in arsenic contaminated areas.

The primary source or the parental outcrops of arsenic in the Ganga-Brahmaputra basin is yet to be established. However, the occurrence of arsenic in groundwater in the BDP and Gangetic plains has been recognized as of geological origin with spread out resulting from the mobilization under natural hydro-geologic conditions. Two hypotheses recommending mechanism of arsenic mobilization in the groundwater, one - oxidation of arsenopyrite or arsenic rich pyrite in soil strata, and the other, reductive dissolution of arsenic from soils, the later case 'the reductive dissolution' is recognized as the most potential reason than the former as the dominant

mechanism of arsenic groundwater contamination. The mechanism states that the As derives from reductive dissolution of Fe oxyhydroxide (FeOOH) and release of its sorbed As. The Fe oxyhydroxide exists in the aquifer in dispersed phases, such as coatings on sedimentary grains. Reduction of the Fe is driven by microbial metabolism of sedimentary organic matter present in the system as C. Identification of the mechanism of As release to groundwater would help to provide a frame work to guide the placement of new water wells having acceptable concentrations of As.

