

Chemistry of arsenic in groundwater of Ganges–Brahmaputra river basin

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The presence of arsenic (As) in water and its effect on human health through both drinking and agricultural practices is of serious concern worldwide. Arsenic-rich groundwater mostly occurs in the Bengal Delta Plain, covering the state of West Bengal, the adjoining country of Bangladesh and extending to Jharkhand, Bihar, Uttar Pradesh, Assam, and other Northeastern states of India and the neighbouring country of Nepal. The number of people at risk of arsenic poisoning, through drinking water from sunken wells, may be considerably larger than previously thought of. This article conceptualizes by reviewing the As sources, major occurrences, mechanisms of arsenic mobilization and process of contamination in groundwater of Ganges–Brahmaputra river basin of India through an integrated approach.

Keywords: Arsenic contamination, arsenic acid, Ganges–Brahmaputra river basin, groundwater.

THE Ganges–Brahmaputra river basin is the 13th largest river basin¹ in the world, with an annual run-off of about 1400 billion m³ and is home to old civilizations². The surface area of the Indian subcontinent is 3.3 million km² and it is separated from the Asian mainland by the Himalayas. The Ganges River System (GRS) in North and eastern India, carries a high sediment bed load. The sediment bed load estimated at 1–2.4 billion tons per year discharges into the Bay of Bengal^{3,4}, thus making 6–16% of global annual sediment flux of about 15 billion tons⁵. The Bengal Delta Plain (BDP) is drained by three important rivers – the Ganges, Brahmaputra and Meghna (G–B–M) – originating from the Himalayas and channelling suspended solids (1060 million tons), water (>1330 km³) and dissolved particulates (173 million tons) to the Bay of Bengal⁶. The Bay of Bengal receives maximum amount of sediments from the G–B–M river system⁷ containing several trace elements, including arsenic. Arsenic is important due to its association with environmental issues and health of humans, animals and plants⁸.

Arsenic distribution in Ganges–Brahmaputra river basin

Arsenic problem in groundwater in West Bengal was first recognized^{9–12} in the late 1980s and the health effects are

now reasonably well documented. More recently, the scale of the problem in other states with similar geology like Assam, Bihar, Uttar Pradesh, Tripura, Manipur, Arunachal Pradesh and Nagaland, has also been reported^{12–15}. The affected aquifers of the region are mainly Holocene alluvial and deltaic sediments, similar to those in large parts of Bangladesh. Geologically, the Bengal basin is in intense neotectonic activity¹⁶, and its west, north and east are bordered by the Indian Shield, Shillong Plateau and Naga–Lusai orogenic belt respectively.

Recent estimates suggest that elevated concentrations of As exist in groundwater of nine districts of West Bengal, namely Murshidabad, Malda, Nadia, North 24 Parganas, South 24 Parganas, Bardhaman, Howrah, Hoogly and Kolkata. Nearly 50 million people living in 3200 villages in nine of the total 18 districts of West Bengal, covering 38,865 km², are exposed^{17–21} to drinking water containing As above 50 µg/l. Rice and vegetable fields irrigated by groundwater receive a large amount of arsenic through shallow tube-wells in the affected areas of North 24-Parganas and Murshidabad, West Bengal^{22,23}. Elevated concentrations of As have been reported from Ganges–Gaghra Plain, Ballia district, eastern Uttar Pradesh^{20,21,24}, Bhojpur, Buxar and Shahebganj districts, Bihar and Jharkhand situated on the western banks of the Ganges^{20,25}. In Northeastern India, arsenic has been detected in 21 of the total 24 districts of Assam and three districts in Tripura, six in Arunachal Pradesh, one in Manipur and two in Nagaland¹⁵. The existence of contamination has been well established in the old Brahmaputra Plain of Bangladesh^{18,26} and field surveys^{21,27}. Maximum As content was observed in Jorhat, Dhemaji, Golaghat and Lakhimpur, Assam; West Tripura, Dhalai and North Tripura districts, Tripura; Thuobal Manipur; Dibang valley, Arunachal Pradesh, and Mokokchung and Mon districts, Nagaland. No detailed information on contamination of groundwater by As is available for the mid and upper Ganges Plains. Hot spots for As contamination at the upper, mid and lower plains of the Ganges have also been reported²¹.

Arsenic sources

Arsenic is a natural constituent of the earth's crust and is the 20th most abundant element. The average concentration^{28,29} of As in the continental crust is 1–2 mg/kg. Arsenic is released in the environment through natural

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processes such as weathering and volcanic eruptions, and may be transported over long distances as suspended particulates and aerosols through water or air. Arsenic emission from industrial activity also accounts for widespread contamination of soil and groundwater environment^{30,31}. Many authors have reported As emissions to the atmosphere on global, regional and local scales³²⁻³⁴. Once introduced into the atmosphere, As may circulate in natural ecosystems for a long time depending on the prevailing geochemical environments³⁵⁻³⁹.

Natural sources

There is limited information on the natural emission of As in the Ganges–Brahmaputra basin. The natural release of As in groundwater in parts of the BDP, West Bengal has been documented, where As is mobilized from the Holocene sediments comprising sand, silt and clay^{40,41}. Arsenic concentration^{28,42} in different sediments could be as high as 490 mg/kg. Several isolated geological sources for 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)^{11,12,43,44}. The source of As contamination in the Ganges–Brahmaputra basin remains to be identified. 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 As^{45,46}. Groundwater of the reducing sedimentary aquifers on the other hand, is characterized by high concentrations of dissolved Fe due to the reductive dissolution of Fe oxyhydroxides that mobilize the sorbed As. Studies on the hydro-geochemistry of the BDP groundwater^{13,43,47} have revealed elevated concentrations of Fe (145–8624 µg/l) in groundwater, whereas Fe concentration in groundwater in Bihar ranges from below detection limit to 700 µg/l. Irrespective of the concentration of Fe in groundwater, the process for its release is triggered by the reduction of Fe oxyhydroxides in the Ganges sediments, with consequent release of As.

Anthropogenic sources

The release of As from different facilities is often cited in the literature^{35,48}, but there is still lack of information on atmospheric emission of As in eastern regions of the Indian subcontinent. Average concentration of As in Indian coal ranges up to 3.72 mg/kg, with a maximum value of 40 mg/kg (e.g. Sohagpur coalfield, Northeastern India)^{49,50}. Hence, it is believed that coal combustion in Eastern India is one of the major sources of anthropogenic As 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 As into the environment. However, there are no data on the exact tonnage of As entering the environment. A secondary lead industry near greater Kolkata, West Bengal, releases As to the environment and maximum concentration in soil of the area is reported⁵¹ to be 9740 ± 226 mg/kg; the minimum is 17.5 ± 0.52 mg/kg. Leaching of As in groundwater is also expected in the vicinity of areas of landfills containing waste and hazardous waste piles^{35,52,53}. The use of fertilizers and insecticides also causes high concentration of As in soil compartments. There is lack of information on the anthropogenic deposition of As within the extensive alluvial tract of the Ganges–Brahmaputra river basin. The As-affected areas are parts of the lower delta plain of the Ganges river and foothills of Brahmaputra and Barak valley, and the sources of As 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 is claimed that the Ganges–Brahmaputra basin is rather undisturbed by anthropogenic sources compared to industrialized countries, where river basins are generally affected by industrial activities⁵⁴.

Major As occurrences in groundwater

In groundwater, inorganic As commonly exists as arsenate (As^{5+}) and arsenite (As^{3+}). Inter-conversion of As^{5+} and As^{3+} takes place by oxidation of As^{3+} to As^{5+} and reduction of As^{5+} to As^{3+} . There is another mode of occurrence of arsenic, namely organoarsenic, which is mostly less toxic than both As^{3+} and As^{5+} . Organoarsenic is formed from inorganic arsenic by a process called biomethylation. Organoarsenic occurs in various organisms such as plants, fish, crab and the human body. Biological methylation or biomethylation is performed by heavy-metal bacteria or fungi which are devoid of chlorophyll, such as prokaryota (bacteria) and akaryota (fungi). The molecular structure of naturally occurring inorganic and organic species of As is presented in Figure 1.

High concentrations of arsenic tend to occur in sulphide minerals and metal oxides, especially iron oxides. Several studies suggest that the As-rich groundwater 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^{40,55}. However, recent studies indicate that the vast tract of Indo-Gangetic alluvium extending further to the west and the Brahmaputra alluvium have elevated concentrations of As 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 oxyhydroxides that precipitated under oxidizing conditions generally prevailing during the deposition of the Holocene sediments. However, redox

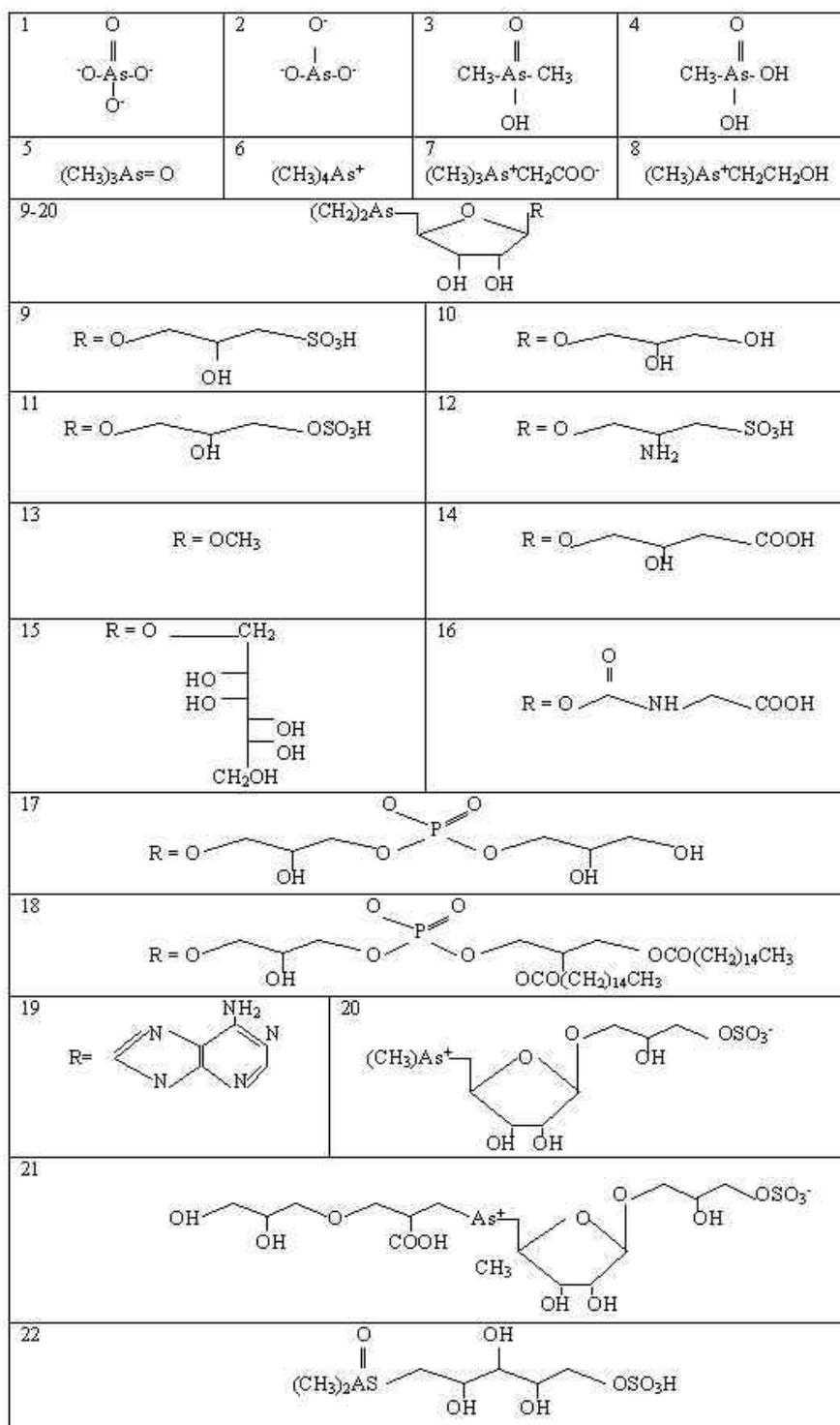


Figure 1. Structure of naturally occurring inorganic and organic arsenic species.

processes in the sediments trigger the reductive dissolution of iron oxides that transfers substantial amounts of As in aqueous phases through biogeochemical interactions^{56,57}. As-containing groundwater in Ganges–Brahmaputra river basin is hosted by the sediments deposited by the rivers during the late Quaternary or Holocene age. Lithology of

these late Quaternary sediments include sands, silt and clay. Mineralogical composition of these sediments consist of quartz, feldspars, illite and kaolinite and the fine-grained overbank facies are rich in organic matter^{58–60}. There is thick layer of newer alluvium containing sand, silt and clay, which spreads out by numerous rivers that originate

from the Himalayas both in the north and northeast. Most environmental arsenic problems recognized today are the result of mobilization under natural conditions.

Mechanisms of As mobilization

Geochemical and hydro-geological characteristics of alluvial sediments govern the mobility of As in groundwater, and the source of As in the sediments depends on the geology of the source terrain³¹. The retention or mobility of As under varying redox (oxidation–reduction) conditions is based on the interaction of the aqueous phase with different mineral phases in the sediments. It has also been reported⁶¹ that mineralogical characteristics of the sediments reflect differential concentrations of As. The mechanism of As release and mobilization in groundwater has been a subject of considerable controversy. Detailed discussions on three contrasting hypotheses have been published^{61–65}. They are:

- Release of As following the oxidation of As-rich pyrite;
- Reductive dissolution of iron hydroxides and release of sorbed As into the groundwater, and
- Anion exchange of sorbed As with phosphate from fertilizers.

Oxidation of sulphide minerals (pyrite-FeS₂) has been advocated strongly by many workers in West Bengal as the cause of groundwater arsenic problems⁶⁷. It is possible that such oxidation processes could be involved in some parts of the aquifers, particularly at the shallowest levels; for instance the depths penetrated by dug wells. However, it is not considered to be the main cause of groundwater arsenic problems in the Ganges–Brahmaputra river basin.

One of the main conclusions from recent research studies has been that desorption or dissolution of arsenic from iron oxides is an important or even dominant control on the regional distributions of arsenic in water⁶⁸. The onset of reducing conditions in aquifers can lead to a series of changes in the water and sediment chemistry as well as in the structure of iron oxides. Many of these changes are poorly understood on a molecular scale. Some critical reactions in the change to reducing conditions and to subsequent arsenic release are likely to be the reduction of arsenic from its oxidized (As⁵⁺) form to its reduced (As³⁺) form. Under many conditions, As³⁺ is less strongly adsorbed to iron oxides than As⁵⁺ and reduction should therefore involve a net release from adsorption sites. Dissolution of the iron oxides themselves under reducing conditions is another potentially important process. Additional influences such as competition from other anionic solutes (e.g. phosphate) for adsorption sites may also be important. Under aerobic and acidic to neutral conditions,

adsorption of arsenic (As⁵⁺) to iron oxides is normally strong and aqueous concentrations are therefore 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 and a resultant increase in dissolved concentrations. Such processes are considered to have been responsible for the release of arsenic in oxidizing Quaternary sedimentary aquifers.

In addition, the role of microorganisms in the leaching of As from sediments has been discussed; As mobilization occurs by microbial degradation in the presence of organic substrates in reducing aquifers^{40,61}. Burial of organic matter along with the sediments facilitates microbial activity, which plays an important role in the generation of reducing conditions^{18,69}. The rates of arsenic release reactions under such conditions are likely to be dependent on a number of factors, including rates of sedimentation, diffusion of gases and microbial reactions, but they are likely to 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^{18,69,70}. 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 As mobilization⁶⁹. Whatever the nature of the organic matter, its importance in controlling the redox conditions in reducing aquifers such as those of the Bengal basin is widely acknowledged.

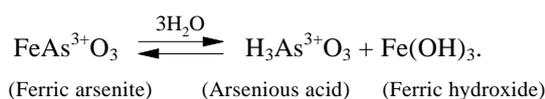
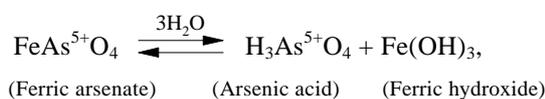
The surface reactivity of iron (Fe) and aluminium (Al) plays an important role in adsorbing the bulk of As in the sedimentary aquifers in the Ganges–Brahmaputra basin. However, it was reported that the theory does not explain increasing As concentration in existing tube-wells, previously safe but now progressively contaminated⁶⁴. Sediment analyses showed that extensive groundwater withdrawal for agricultural purposes favours the oxidation of As-rich iron sulphide and thereby mobilizes As in the Bengal basin^{62–64}. Adsorption to hydrous aluminum and manganese oxides may also be important if these oxides are present in significant quantity^{71,72}.

It was speculated that phosphate concentrations in groundwater of the BDP resulted from application of fertilizers^{12,43}, but this is unconvincing because the amount of dissolved and sorbed phosphate in the aquifer volume exceeds the amount of phosphate applied as fertilizer⁴⁷. Increased use of water for irrigation and use of fertilizers have caused mobilization of phosphate from fertilizers down to the shallow aquifers, which has resulted in the mobilization of As due to anion exchange onto the reactive mineral surfaces. Since phosphate is bound strongly onto these surfaces, As⁵⁺ can be mobilized in groundwater¹². However, it was confirmed that phosphorus

in groundwater cannot contribute to As pollution by experimental desorption by phosphate of As sorbed to mineral surfaces⁷³. However, microbiological and chemical processes might increase the natural mobility of As⁴³. Recently, a new hypothesis based on displacement of As by dissolved bicarbonate as an alternative mechanism for the genesis of high-As groundwater has been proposed⁵⁷. However, all these hypotheses have their own discrepancies and hence, there is a need for integrated research in order to understand sources, release mechanisms and mobilization of As in sedimentary aquifers.

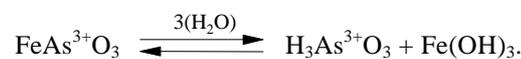
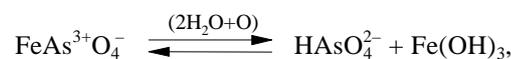
Process of arsenic contamination

Iron arsenate (FeAsO₄) may be tentatively regarded as the direct and immediate source of arsenic, because it is easily formed from scorolite [FeAs₄, 2H₂O] and pitticite (hydrated mixture of arsenate and sulphate), which are common alteration products of arsenopyrite. Since arsenopyrite can contain As³⁺ ions in small proportion with ions of As⁵⁺ which is the dominant constituent, it is quite likely that arsenic in the alluvium occurs as ferric arsenate (FeAsO₄), with ferric arsenite (FeAsO₃) in minor proportion. Due to hydrolysis under conditions of low pH and high Eh, ferric arsenate is dissociated into the strongly poisonous arsenic acid (H₃AsO₄) with ferric hydroxide, whereas ferric arsenite breaks down into arsenious acid (H₃AsO₃) and ferric hydroxide. The relevant equations for such hydrolysis are as follows:

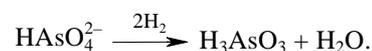


Ferric hydroxide is soluble in acidic aqueous environment, but it is precipitated in alkaline and reducing conditions at low Eh. Thus, if the acidity of the solution decreases (pH increases), colloidal precipitation of ferric hydroxide take place. Some As⁵⁺ and As³⁺ ions being absorbed on the particles of Fe(OH)₃, may be co-precipitated with the latter. This reduces arsenic content of water. However, precipitation of As⁵⁺ and As³⁺ is not simultaneous because As³⁺ is 5 to 10 times more soluble than As⁵⁺ and its stability in aqueous solution increases with the alkalinity of water and reducing character of the environment. Thus, even after colloidal precipitation of As⁵⁺ ions with ferric hydroxide, the aqueous solution may contain As³⁺ 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 As⁵⁺-bearing arsenic acid

(HAsO₄²⁻) and As³⁺-bearing arsenious acid (H₃AsO₃) respectively, together with ferric hydroxide in both cases. The relevant equations are:



Arsenous acid (HAs⁵⁺O₄²⁻) is the commonest of arsenate compounds in natural water as aqueous solution. In a mildly reducing environment, HAsO₄²⁻ is converted into As³⁺-bearing arsenious acid (H₂AsO₃¹⁻) and in a strongly reducing condition into arsenious acid (H₃AsO₃). The change can be shown by the following equations:



In the absence of As³⁺ in the source material (FeAsO₄), As⁵⁺-bearing arsenic acid (HAsO₄²⁻) can be formed by the hydrolysis of FeAsO₄ in a mildly alkaline and oxygenated environment and ferric hydroxide is produced at the same time.

In the biomethylation process (Figure 2), arsenic in the sediment is hydrolysed to arsenic acid and is further reduced by bacteria to As³⁺O(OH) forms arsenite in solid state. Thus the first role of bacteria is to increase the ratio of As³⁺/As⁵⁺ in the sediment. This As³⁺ readily goes into aqueous solution to increase As toxicity of water. The next step of change brought about by bacteria is biomethylation of As³⁺O(OH), resulting in the formation of CH₃As⁵⁺O(OH)₂ or methyl arsenic acid and (CH₃)₂As⁵⁺O(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 (CH₃)₃As³⁺ or trimethylarsine by aerobic bacteria under oxidizing condition, whereas, anaerobic bacteria under reducing condition convert cacodylic acid to (CH₃)₂HAs³⁺ or dimethyl arsine. Both are soluble in water and are toxic. The biomethylation process increases the proportion of organoarsenic, 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 in-

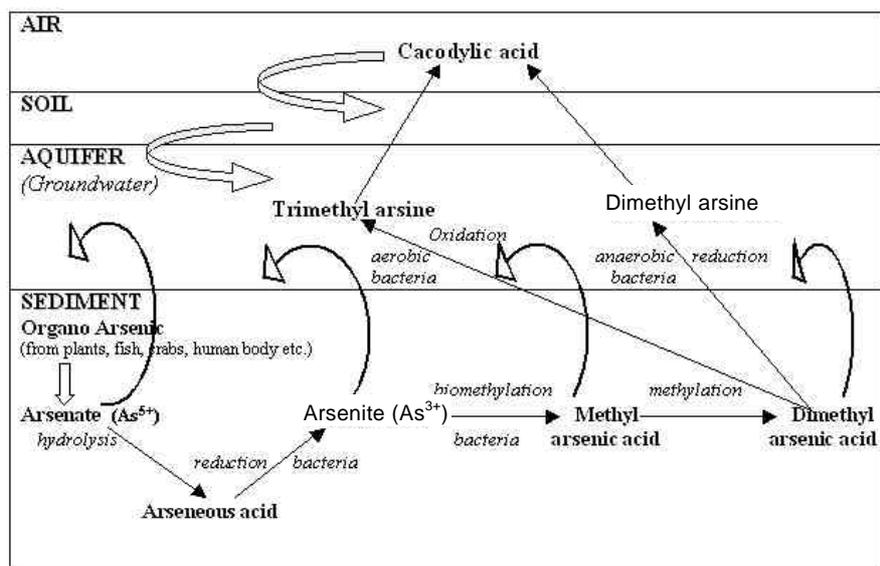


Figure 2. Organoarsenic cycles in sediments.

tensity of rainfall in the catchment 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 more sandy and periodic fluvial action keeps the alluvium stratified. However, its influence has been gradually obliterated by climate as one moves 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, As elements get released in the reducing environment by the process of biomethylation and get shelter within silty and clayey sediments. Some studies^{40,58} 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 practised 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.

Most experts agree that the source of such high arsenic anomaly in groundwater is geological rather than from pesticide or other artificial sources. It is postulated that arsenic-bearing sulphide minerals, the commonest of which in nature is arsenopyrite (FeAsS) and/or their 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 As pollution, the relation between chemistry of arsenic and high arsenic anomaly in groundwater is an interesting subject of study.

Conclusions

- (i) Part of the arsenic contamination in a vast area of the Ganges and Brahmaputra basin (West Bengal, Northeastern states, Bihar, Jharkhand and Uttar Pradesh) is possibly mainly geological.
- (ii) The immediate source material for groundwater is likely to be ferric arsenate (with or without ferric arsenite) derived from an alternation product of the mineral arsenopyrite that was geologically transported to the Bengal delta and Assam valley.
- (iii) Contamination takes place by chemical and biological processes that lead to the formation of arsenic acids from buried arsenate. The plausible chemical process is hydrolysis of arsenate.
- (iv) Supply of excess oxygen during withdrawal of groundwater from tubewells appears to be responsible for hydrolysis.
- (v) There is a need for integrated research to understand sources, release mechanisms, mobilization of As in aquifers and the chemistry of arsenic and high arsenic anomaly in groundwater of the Ganges and Brahmaputra river basin.

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