Groundwater arsenic pollution affecting deltaic West Bengal, India

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Late Quaternary stratigraphy, geomorphology and sedimentation in the Bengal Delta and the Damodar fan-delta have partly controlled groundwater arsenic contamination. The arsenic pollution is extensive at shallow depth in the low-land organic-rich Holocene sediments characterizing the southern parts of the Bengal Delta. The upland terraces within the Bengal Delta, mainly made up of the Pleistocene sediments topped by an oxidized impervious zone, are free of arsenic problem. These uplands extend as regionally persistent palaeo-interfluve areas dissected by Holocene sediment filled palaeochannels. The groundwater in palaeochannels is polluted in absence of protection by the impervious Pleistocene cover. The arsenic contamination in the Bengal Basin is geogenic and sourced mainly from the Himalaya. The Gondwana coal and minor sulphide occurrences from the Peninsular India might be sources for arsenic pollution in the Damodar fan-delta. No arsenic mineral is present in arsenic contaminated alluvial aquifer; instead arsenic occurs adsorbed on hydrated ferric oxide (HFO), which generally coat clastic grains. Arsenic is released to the groundwater mainly by bio-mediated reductive dissolution of HFO with corresponding oxidation of organic matter. Arsenic often remains locked in alluvium and not released to groundwater. Therefore, the release process is more important factor causing arsenic pollution rather than source.

Keywords: Arsenic in groundwater, Bengal Basin, Holocene sea level rise, source and release of arsenic, West Bengal.

Introduction

ARSENIC toxicity in groundwater has affected major parts of the Bengal Basin covering Bangladesh and southern West Bengal1–4 (Figure 1) as well as other parts of the world5–6. It is a major environmental problem affecting Bengal. The presence of arsenic in groundwater exceeding the permissible potable limit of 50 μg/l was recorded in West Bengal in 1978, and initial cases of arsenic poisoning was diagnosed in 1983 (ref. 7). The recommended limit of arsenic in potable water has been lowered to 10 μg/l by the Bureau of Indian Standards8.

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Within a span of 20 years, around 9.5 million people in nine districts in southern West Bengal were affected. The Geological Survey of India during 1954–1959 quantitatively assessed groundwater potential for irrigational use9. To increase food growth through groundwater irrigation, private individuals were encouraged to meet their need through sinking shallow tube-wells, but unfortunately without assessment of availability and monitoring over the activities. This resulted in over withdrawal, misuse and abuse of groundwater resource. During the past 40 years, groundwater has been increasingly used for irrigation and the use of phosphate fertilizers has increased manifold. More than 0.5 million tube-wells with hand-pumps, 0.1 million shallow tube-wells and 3000 deep tube-wells were sunk10,11 at depths of 10–20 m, 30–100 m and 50–200 m respectively till 1996. Widespread withdrawal of groundwater possibly triggered mobilization of degraded organic chemicals and phosphates into the aquifer system12,13. This in turn promoted growth of sediment biota as well as reduction and dissolution of the hydrated iron oxide and desorption of arsenic from the sediments to the groundwater14,15. It is an irony that arsenic toxicity from Bangladesh and West Bengal was recognized after making huge investments.

Figure 1. Map showing arsenic-contaminated areas in India15–20. 1, Indo-Ganga-Brahmaputra alluvial plain; 2, Bengal Basin; 3, Dongargarh rift zone in hard-rock area. Abbreviated locality: B, Ballia; BG, Bhagalpur; BH, Bhutan Hills; BX, Buxar; C, Chhapra; CP, Chhotanagpur Plateau; H, Hazaribagh Plateau; K, Kolkata; P, Patna; UA, Uttarakhand Hills; A, Allahabad; CH, Chandigarh; M, Meerut.

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Groundwater irrigation for high-yielding ‘Boro’ rice and a switch to multi-crop practices achieved ‘Green Revolution’. Groundwater-based piped water supply also reduced infant mortality from diarrhoeal diseases. Unexpectedly, however, the practice also ushered in arsenic malady to deltaic and parts of flood-plain domains of the Ganga–Brahmaputra river system.

The arsenic-affected deltaic plains of Bengal and other such areas are free of any industrial, mining or geothermal activities and represent natural geological settings. The nature and disposition of arsenic pollution in West Bengal is reviewed in this article. Arsenic-contaminated area is mainly confined to the east of the Bhagirathi River (also known as Hoogly River), which is the principal distributory of the Ganga River. Contrary to an earlier report, some arsenic-contaminated areas have been located over the Damodar fan-delta (Figure 2), which is exclusively confined to the Peninsular India.

Bengal delta plain

The Bengal delta plain is extensively affected by groundwater arsenic pollution, which mainly affects lower grounds comprising the Holocene deltaic sediments, whereas the Older Alluvial uplands and interflue areas are generally unaffected. It is thus necessary to know the morphostratigraphic setting of the Bengal delta plain.

The rivers Ganga, Brahmaputra and Meghna, fed by the tributaries from the Himalaya, the Peninsular India and the Indo-Burma Range flow into their combined Bengal delta (Figure 1). It spans ~1.4 × 105 km² in area and covers most of Bangladesh and parts of West Bengal, India. Main problems in reconstruction of the Quaternary stratigraphy of the Bengal Basin, as common with many other alluvial basins, are lack of subsurface data, monotonous lithology without any marker beds and the paucity of datable material and dates. The Bhagirathi River has scoured its recent and immediately older deltaic basins during the Quaternary sea level fluctuations. Four geomorphic and morphostratigraphic units have been identified in West Bengal and the bordering Bihar and Jharkhand states. The western uplands of undulating hills of older rocks framing the delta are divisible into three stepped alluvial plains: e.g., western belt of undulating hills of older rocks, the Laterite Plain, the Older Alluvial Plain (OAP) and the Younger Delta Plain (YPD) respectively of the Bhagirathi–Ganga river system (Figure 3). These units gradually come down in elevation in the east and southeast. Based on integrated analysis of these morphostratigraphic units and a few borehole records, subsurface extension of some of these units has been established to marginal parts of the Bengal Basin, whereas several Holocene subsurface units beneath YDP do not outcrop. The presence of characteristic soil profiles, e.g., laterite/ferrisol, calcrite recognized at subsurface has helped such correlation. The areas covering ODP and older surfaces are free of arsenic contamination, which affects parts of YDP, occurring mainly to the east of the Bhagirathi River. The base of the Quaternary

Figure 2. Geomorphologic and Quaternary morphostratigraphic map west of Bhagirathi River, West Bengal. Morphostratigraphic units: 1. Laterite Plain (Pleistocene); 2, Kusumagram Plain (Older Delta Plain, Pleistocene–Holocene); 3, Karna Plain (Younger Delta Plain, Holocene); 3A, Damodar fan-delta plain; 3B, Bhagirathi delta plain; 3C, Valley cuts in 2; 4, Recent Bhagirathi Plain. Gp, Gutipara; Ng, Natagarth, Bg, Balagarth.
section is difficult to identify, but in many boreholes a sequence dominantly of clay and sand having saline formation water and locally containing microfossils have been assigned Upper Pliocene age. The presence of the Youngest Toba–Ash Bed marker \(^{20}\) (75,000 yrs BP) has been recorded from basal parts of the Quaternary profile from the Brahmani and the Barakar river sections, located west of the Bengal Basin margin. These beds are tentatively correlated with the younger laterite topped Quaternary unit, which may be tentatively assigned Pleistocene–early Holocene age, whereas the OAP deposits to its immediate east are early Holocene in age \(^{13,15,16}\).

The sedimentation in the Bhagirathi–Ganga delta plain was strongly influenced by the sea-level changes during the Late Pleistocene and Holocene \(^{19,21-24}\). The OAP deposits from the West Bengal are truncated, incised and superposed by the lower level terraces of YDP, which in turn is incised by the present channel and floodplains of the river Bhagirathi (Figure 4). The tributaries responsible for the deposition of OAP in the West Bengal had their courses at high angle to the present Bhagirathi course. Parts of OAP fill have been eroded and parts dip beneath the western cover of YDP. The Holocene sediments beneath YDP in the West Bengal and Bangladesh have been tentatively classified into three broad stratigraphic units (Figure 5) based on limited subsurface data \(^{13,15,25,26}\). It must be recognized that being alluvial units these stratigraphic units are not layer cake in geometry. Thus at places Late Pleistocene sediments can occur at shallow depth and incised Holocene sediments may occupy deeper levels. The near surface unit 3 consists of mud, silt, fine sand and locally present peat beds; unit 2 is dominantly composed of fine, often dirty sand with clay intercalations; whereas the unit 1 is coarser, cleaner and sandy. Most arsenic polluted tube-wells generally tap aquifers in unit 2. \(^{14}C\) ages in organic matter from the basal unit 1 range from 28,300 to 12,300 yrs BP. The basal sand and gravel-bearing unit 1 was deposited in entrenched palaeochannels during the Late Pleistocene and the earliest Holocene under low-stand setting \(^{13,15,17,22-25}\). Sea-level gradually decreased and reached their lowest level of ~135 m during the Late Pleistocene around 18,000 yrs BP, when the Pleistocene and Late Tertiary sediments located in the present Ganga delta and shelf areas were exposed to erosion and oxidation. Parts of the Pleistocene cover around the present delta region remained as incised upland terraces, which were dissected by the proto-Bhagirathi–Ganga–Brahmaputra river system. The Pleistocene terraces, topped by oxidized sediments and hard brown-blushy gray impervious clay palaeosol formed interfluvе uplands. These were dissected by Holocene sediment filled palaeochannels and in turn partly buried under younger deltaic Holocene sediments. The hard clayey aquitard corresponding to the Last Glacial Maximum Palaeosol (LGMP) strongly influenced groundwater flow and controlled location of arsenic.

**Figure 3.** Landforms and depositional environments in parts of Bengal Basin \(^{12,22}\). B, Barind; M, Madhupur; L, Lalmai (Pleistocene uplands). Abbreviated locality: B, Balagarh; K, Kolkata; G, Ghatugachhi; Dk, Dhaka; M, Malda; Rn, Ramnagar.

**Figure 4.** Palaeogeographic block diagrams of parts of Bengal Basin during Holocene \(^{15,25}\).
pollution to shallow aquifer in the Bengal Delta\textsuperscript{13,25,27}. Selected studies in Nadia and North 24 Parganas districts in South West Bengal and elsewhere revealed that groundwater in palaeochannel is polluted by arsenic, whereas those in and beneath palaeo-interfluve areas remained free of pollution. Groundwater in latter areas are protected by IGMP, preventing downward migration of arsenic and downward migration of organic matter that drives arsenic release to groundwater.

The basal sand and gravel unit was not uniformly developed, but was mainly restricted to palaeochannel floors (Figure 3). From 18,000 to 12,000 yrs BP, the sea level continued to rise causing transgression overlapping sedimentation that filled entrenched valleys with fluvial or fluvio-deltaic sand, silt and clay. Some of these sediments were also directly deposited over the eroded and oxidized Pleistocene or Upper Tertiary sediments in the delta plain and surrounding area.

Based on \textsuperscript{14}C ages from various levels of unit 2 and base of unit 3, the age of unit 2 has been broadly inferred to be 10,000–7,000 yrs BP\textsuperscript{13,15,24,25}. The sea level rose continually till 9500 yrs BP, to reach ~20 m level and then broadly maintained this level till 7000 yrs BP\textsuperscript{24,25}. The rising sea level at the initial stages would have flooded the partly sediment covered entrenched valley courses of the proto-Bhagirathi and the Ganga–Brahmaputra rivers, and converted their lower and adjacent parts to fluvial marshes, lagoons and estuaries (Figures 3 and 4). A swamp would be formed ahead of the rising sea level. High tides in the Bay of Bengal would advance the tidal flat and mangrove growth to invade the delta mouth, which would clog with mud and silt rich in organic content. Thus, clay and silt that are rich in organic matter and interbedded with lenticular sand bodies from numerous transient tributary channels dominated the middle unit.

The sea-level again began to rise rapidly between 7000 and 5500 yrs BP, reaching higher than the present level and southern parts of the Ganga–Bhagirathi delta were invaded further by tidal mangrove and encroached by the Bay of Bengal. The sea level subsequently dropped initiating a phase of subdued marine regression. The unit 3 in the Bhagirathi–Ganga delta from West Bengal and Bangladesh is ~7000 yrs BP, and younger in age. Typical estuarine brackish to freshwater environment have been reported from the clay-rich sediment in and around Kolkata and close to the western bank of the Bhagirathi River and south of the Damodar fan-delta, southern West Bengal. These sediments occur at 7–2 m beneath bgl. There was widespread development of marine and freshwater peat layers around Kolkata and about 60 km further north during 7000–2000 yrs BP\textsuperscript{21}.

**Damodar fan-delta**

Some parts of the Damodar fan-delta are found to be affected by groundwater arsenic pollution\textsuperscript{17}. The provenance of this basin is entirely confined within the Peninsular India and had no Himalayan influence. The setting of this area thus assumes importance although only a few isolated areas are affected by groundwater arsenic pollution.

The Damodar river was flowing east to meet the Bhagirathi River during the middle of 18th century, but it has since rotated its course over its fan, shifting its mouth 128 km to the south. The Ajay river located further north, still flows east to meet the Bhagirathi river, which was the regional slope that was followed by the older proto-Damodar and other tributary rivers of the western upland\textsuperscript{19}. The Bhagirathi River system continued to remain to the east of the proto-Damodar and the Damodar
fan. Morphostratigraphic units of the Damodar fan-delta are shown in Figure 2.

Although arsenic-affected areas are mainly located to the east of the Bhagirathi river, several areas west of the Bhagirathi River are also arsenic affected. Many affected areas in the Balagarh Block are located over the Damodar fan-delta, where maximum arsenic concentrations of 85–90 µg/l have been recorded. The arsenic-affected areas in Amta and Bagman Blocks are located on either side of the present Damodar channel but south of the toe of the Damodar fan-delta. Amta and Bagman areas record maximum arsenic concentration of 50 and 90 µg/l respectively. The contaminated aquifers occur at depths 10–40 m corresponding to unit 2 being located significantly below the clayey carbonate zone bearing unit 3 recorded in several tube-wells (Figure 6).

Source and release of arsenic to groundwater

No specific sources of arsenic could be identified from the affected alluvial areas, e.g. Bhagirathi–Ganga delta, Damodar fan-delta. One of the main problems in depicting the source of arsenic in alluvial domain is the mobile nature of the element, which can be easily removed from the source during the alteration process, and then transported in water either in solution or in suspension adsorbed onto various phases, e.g. Fe–Mn hydroxide, mica, clay, organic matter or recombine with phases of sulphides, or Fe–Mn hydroxide, before being scavenged and mobilized to groundwater.

It was earlier believed that the opaque particles in the aquifer sediments are the source of arsenic that was erroneously inferred to be arsenic-rich pyrite. Nickson et al. on the other hand, suggested that arsenic is derived from sulphide deposits in the Ganga Basin such as the copper belt of Jharkhand (erstwhile Bihar) and the Gondwana coal basins of the Damodar valley. The suggested potential sources by Nickson et al. are located far south of the arsenic-affected Ganga tributary system. Acharya et al. listed sulphide occurrences, some of which are arsenic bearing, from the Himalayan foothills, e.g. Darjeeling, Bhutan and Uttarakhund as well as from the Peninsular India, e.g. Anjore pyrite deposit from the Vindhyan hills and Son valley gold belt, that borders the southern parts of the Middle Ganga plain. These could be potential sources for arsenic in the Bengal basin. Since the southern belt of the Himalayan range is subjected to high erosion and intense rainfall during the Holocene, it is possible that these minor occurrences might have transported arsenic-bearing products to the Ganga floodplain and the Bengal delta. Further, arsenic concentrations in biotite–chlorite bearing silt fraction, from the Terai areas of the Ganga, the Tista and the Brahmaputra rivers, are generally higher than normal. Acharya et al. also reported virtual absence of pyrite or any arsenic minerals in the contaminated aquifer (Figure 7).

The Damodar River system located mainly between the Chhotanagpur and the Hazaribagh plateaus exclusively belongs to the Peninsular India (Figure 1). The Gondwana coal basins, minor arsenic mineralization in mica-belt in
the Hazaribagh plateau and minor sulphide occurrences in the Chhotanagpur plateau might account for mild arsenic contamination affecting the Damodar fan-delta17.

Mineralogical studies on sediment cores and tube-well sludge from arsenic affected and unaffected adjacent areas in the Bhagarath-Ganges delta and the Damodar fan-delta corroborate that arsenic-rich pyrite or any other arsenic minerals are rare or absent (Figure 7). However, rare presence of biogenic pyrite is recorded in reducing environment often in association with degraded plant remains13,16,30,31. Biogenic pyrite often grows along clastic grain boundaries and as cement like overgrowth on magnetite (Figure 8). Arsenic-bearing nature of biogenic pyrite indicates co-precipitation and sorption of arsenic in pyrite. These biogenic pyrites therefore have locked arsenic and thus acted as sinks and not sources of arsenic in groundwater13,15,32.

Studies on cores of aquifer sediments from contaminated and adjoining safe zones from Chakda (23°04’ : 88°35’) and Baruipur (22°23’ : 88°27’) areas, West Bengal, revealed no drastic change in mineralogical composition. Sediment fractions of iron-oxide-coated quartz and clay (illite) grains, iron–manganese–siderite, magnetite and biotite/chlorite are found to be arsenic bearing. These fractions are relatively more dominant in arsenic-affected aquifers. Sediment samples from parts of the Balagarh block and over the Damodar fan-delta also reveal similar character17.

Mobilization of arsenic in natural water is a function of local geology, hydrology and biogeochemical characters of the aquifers15–16. The oxidation of pyrite and arsenopyrite under oxic condition mobilizes arsenic and produces acid thus developing low pH and increasing concentration of Fe and SO₄ in groundwater. The release of arsenic to groundwater in the Bengal Delta was inferred due to oxidation process28,29. This is unlikely as pyrite or any other arsenic mineral are absent or rare in these alluvial aquifer sediments. Instead, release of arsenic to groundwater in alluvial aquifer is inferred to be caused by reductive dissolution of iron oxyhydroxide mediated by biota31,32. Also, many fold increase in application of phosphate fertilizer may also cause desorption of arsenic from alluvial sediments to groundwater12,13. Biomediated reductive dissolution of hydrated iron oxide (HFO) that occurs mainly as adsorbed coatings on sediment grains and corresponding oxidation of sedimentary organic matter is regarded as the main mechanism13,32. The biogeochemical reduction process mobilizes arsenic to groundwater from aquifer sediments35–37. Arsenic sorbed in discrete phases of hydrated Fe–Mn oxide was preferentially entrapped in shallow aquifers of argillaceous, organic-rich Holocene floodplain and deltaic sediments. The organic products could be sediment derived or of recent anthropogenic origin38.

Anaerobic heterotrophic Fe³⁺ reducing bacteria (IRB) preferentially reduce and dissolve least crystalline discrete phases of HFO16,33,34. Ferrous ion, released by IRB from sediment coatings of HFO or other Fe-bearing mineral phases possibly reacted with abundantly present bicarbonate in groundwater to precipitate siderite concretions, which grew around sediment grains and/or centres of IRB colony39. Colony-like aggregates of Fe–Mn–siderite concretions and framboidal pyrite (Figure 9).
have been recorded from aquifer sediments from Balagarh and Chakda area respectively, as well as elsewhere. Biogenic objects a few micron in length and less than a micron in width occur inside some of these concretions, which recorded the presence of bacteria. Reduction of HFO is common and intense in affected aquifers in the Bhagirathi–Ganga delta plain as indicated by high maximum concentration of dissolved Fe (5–9–36 mg/l) in contaminated groundwater with maximum arsenic concentration reaching around 1000 μg/l. Even within such arsenic-aFFECTed areas, dugwells are found to be arsenic safe. Thus dug-wells are potential source of arsenic-free water.

The chemistry of arsenic-aFFECTed tube-well water in West Bengal and Bangladesh is invariably based on studies of mixed samples from different depths. An inflatable packer-straddle-pump assembly was used to test the chemical and microbiological characteristics of aquifer water from specific depth from an experimental tube-well (23°04’3; 88°35.1’) in Chakda area. Interpretation of sediment and water analysis indicates that iron-reducing conditions have developed at several levels together with the presence of iron-reducing bacterial activity, where reduction of hydrated-ferric oxide was able to mobilize arsenic from sediment to groundwater.

Although arsenic is present in the sediment throughout its depth in the borehole, it did not have any relation to release of arsenic to groundwater, which was entirely controlled by reducing conditions and iron-reducing bacterial activity. Nitrate and sulphate-reducing conditions were not capable of releasing arsenic. Clayey lenses in the aquifer created low permeability zones, preventing fresh nutrients like nitrate and sulphate to reach these levels where iron-reducing conditions prevailed and released arsenic.

Preliminary results of CO₂ and CH₄ in tube-well water from parts of the Bhagirathi–Ganga delta and the Damodar fan-delta suggest that the process of release of arsenic from hydrated iron oxide is triggered by the activities of anaerobic bacteria in a reducing environment with consequent production of CH₄ with distinctly depleted isotopic character.

Conclusions

Groundwater arsenic contamination in the Bengal delta and the Damodar fan-delta is influenced by common geomorphological setting and sedimentation pattern associated with the Pleistocene–Holocene sea-level changes. Shallow level arsenic-contaminated aquifers of the Holocene age are extensive over the low-lying Bengal delta and lower parts of the Damodar fan-delta. The Pleistocene sediments capped by aquiferic palaeosol and oxidized zone, and sediments beneath them are free of arsenic contamination. The low-stand setting during the Late Pleistocene caused prolonged erosion, weathering and oxidation of sediments that capped the interfluve uplands. The uplands were dissected and entrenched by palaeochannels, which were filled by organic-rich Holocene sediments, and became prone to arsenic pollution. Aquifer sediments in the Bengal delta are mainly derived from the Himalaya with minor inputs from the Peninsular India. Groundwater arsenic contamination in the Damodar fan-delta establishes presence of arsenic source in the Peninsular India. Arsenic-bearing pyrite or any other arsenic minerals are virtually absent in the affected aquifer sediments. Arsenic instead occurs adsorbed on HFO, which preferentially enriched fine grained fluvial and deltaic sediments and occurring as coatings on clastic grains and organic matter.

Arsenic-contaminated groundwater is reducing in nature and in general enriched in Fe and Mn. Release of arsenic to groundwater is mainly caused by the reducing dissolution of HFO and corresponding oxidation of organic matter. Groundwater flow, particularly during the recharge of aquifers, mobilizes dissolved organic matter, contributed by aquifer sediments or by recently accumulated biomass. These products are thus brought in contact with HFO, promoting bio-mediated reductive dissolution and thereby release of iron and arsenic to groundwater. The importance of reduction and microbial state of groundwater in release of arsenic was corroborated by analysis of sediment and water samples from specific depths in an experimental tube-well in Chakda area, West Bengal. It was observed that iron-reducing conditions had developed at several levels and these in presence of iron-reducing bacterial activity caused reduction of HFO and mobilization of arsenic to groundwater. Although arsenic is present in the sediment throughout the depth of the borehole, it did not have any relation to release of arsenic to groundwater.

The recognition of a regionally persistent but discontinuous Late Pleistocene palaeosol aquitard and oxidized sediments at shallow depth, as a potential locale of arsenic-free water within the pervasive arsenic polluted Bengal delta and elsewhere is an interesting derivation, which requires further study. Another practical utility of arsenic release mechanism is the arsenic safe nature of dug-well water because of its oxygenated nature even in arsenic-polluted areas.


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