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Arsenic contamination in groundwater affecting major parts of southern West Bengal and parts of western Chhattisgarh: Source and mobilization process

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Arsenic contamination problem in West Bengal and in Chhattisgarh is a natural phenomenon. The main sources of arsenic in the latter area are in weathered acid magmatic rocks of the Dongargarh rift belt and not from locally present sulphides. In West Bengal, arsenic-sorbed in Fe-oxyhydroxide was preferentially captured in argillaceous, organic-rich, mid-Holocene deltaic sediments. Arsenic concentrations are neither high nor very different between adjacently located polluted or unpolluted aquifers. Arsenic is released to groundwater in both cases by bio-mediated reductive dissolution of Fe-oxyhydroxide. In West Bengal, continued and increased recharging of shallow aquifer because of extensive pumping triggered the reduction process, by inducing and enhancing movement of groundwater having highly reducing degraded organic products.

ARSENIC contamination in groundwater and related diseases affect major parts of Ganga delta down stream of Rajmahal hills in West Bengal, India and other low-lying areas in Bangladesh[1–5] (Figure 1). Alluvial areas from USA, Hungary, China, Taiwan and Vietnam are also similarly affected[6–8]. The problem has also been reported recently from Kaurikasa area, Chhattisgarh[9–13] (Figure 2). Some fear that the manifestation may contaminate Seonath river and groundwater, endangering well-populated townships like Drug, Rajnandgaon and Raipur[10,11]. Arsenic-affected areas in Bengal Basin and Chhattisgarh virtually do not have industrial, mining or thermal water activities as many other affected areas[6–8,14–16]. Results of our studies on this problem in West Bengal and Chhattisgarh are presented here.

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There are two contending schools on arsenic contamination in the Bengal Basin: (1) It is caused by oxidation of pyrite and arsenopyrite that are present in aquifer sediments, by atmospheric oxygen which enters the groundwater due to lowering of the water table caused by excessive groundwater abstraction[1–3,17]. (2) It is caused (in Bengal and other alluvial aquifers) by reductive dissolution of ferric-oxyhydroxide that contains sorbed arsenic[4,18–23].

Enormity of arsenic problem in the Bengal Basin has prompted reversion to surface water-based supply in many affected areas. Such a policy shift will involve enormous financial outlay and would nullify the investment of around Rs 10,000 crores already made in West Bengal alone over the last 30 years. It is necessary that such major policy shift should not be ad hoc, but a science-driven decision[24,25].

A strong correlation exists between the distribution of arsenic-affected area in Bengal Basin and palaeogeomorphology and Quaternary stratigraphy[22,24]. The arsenic-prone low-lying alluvial basin of the Ganga river system, downstream of Rajmahal hills, was entrenched and incised over the Pleistocene uplands during low-stand setting of latest Pleistocene age. The Pleistocene terraces and uplands flanking the western side of the delta and those to the north, northwest and central part of the Bengal basin (Barind and Madhupur tracts) exposing older oxidized and the overlying early Holocene sediments are free from arsenic contamination. The basal sandy fills of entrenched channels are also generally free from such contamination. Dominantly argillaceous and organic-rich fluvio-deltaic sediments that were deposited during the high-stand setting of mid Holocene age (10,000–7500 yr BP)[22–24] are arsenic-prone. The period beginning with 10,000 yr BP, initia-

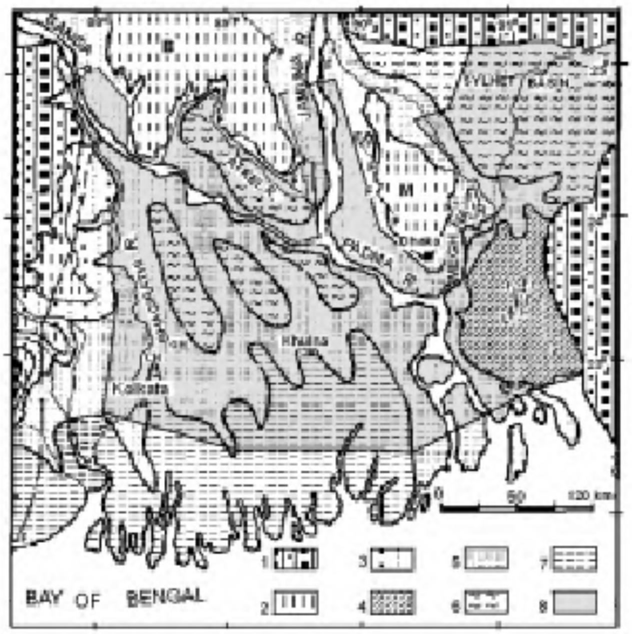

Figure 1. Landforms and morphostratigraphic units in parts of arsenic-affected Bengal Basin (location shown in Figure 2 (inset)). B, Barind; M, Madhupur; L, Lalmai (Pleistocene uplands); CH, Chuchraghat, GH, Ghetugachhi; 1, Hills of older rocks; 2, Laterite/Ferisol Pleistocene uplands; 3, Older alluvial plain; 4, Tippera surface; 5–7, Younger flood and deltaic plain; 5, Undifferentiated; 6, Interdistributary swamp; 7, Tidal swamp; 8, Arsenic-affected area (over parts of 4–7).

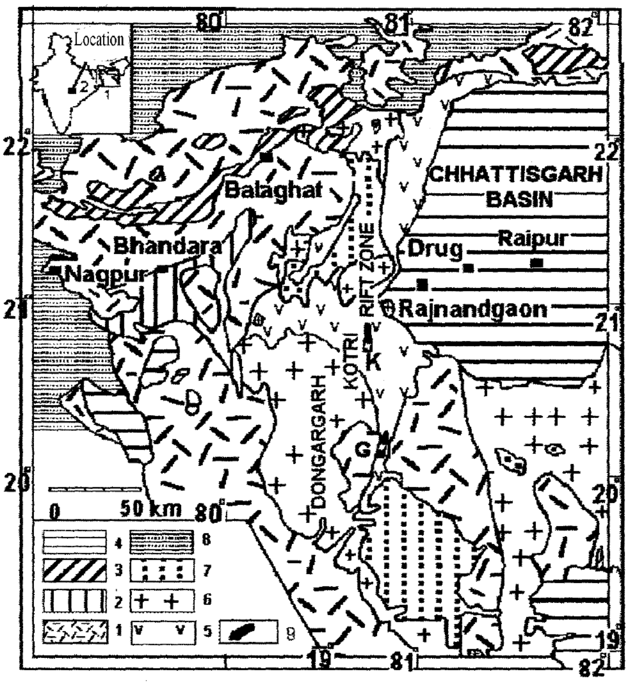

Figure 2. Geological setting of Dongargarh–Kotri rift belt and Chhattisgarh Basin (inset shows location). K, Kaurikasa; G, Gurwandi; 1, Basement gneisses; 2, Sakoli Group; 3, Sausar Group; 4, Chhattisgarh Group sedimentaries; 5–7 Rocks of Dongargarh–Kotri rift belt; 5, Meta volcanics; 6, Granite; 7, Sedimentary cover; 8, Deccan trap; 9, Arsenic-affected area around K and G.

ted Ganga–Brahamaputra delta sedimentation as transgressions back-flooded and over-topped entrenched alluvial channels[26]. Organic matter-rich clay-silt and inter-bedded lenticular sand bodies from numerous transient distributory channels characterized this unit. The peat bearing late Holocene sediments were deposited during high-stand (7000–2000 yr BP), when the sea level was higher than the present one[22–24].

The patchy and isolated arsenic affected areas in Chhattisgarh are restricted to the Dongargarh–Kotri rift zone of Early Proterozoic age (Figure 2). The belt exposes acid and basic volcanics, volcanisediments and intrusive co-magmatic and contemporaneous Dongargarh granite[27–30]. Quartz reefs that are emplaced along several N–S and NW–SE trending shear zones often carry sulphides. The uppermost unit of the rift is a volcanogenic-sedimentary cover. Kaurikasa, Joratarai, Sonsayatola villages located in the northern part of the rift are most affected[9–13], whereas Gurwandi and a few other villages in the southern part are also affected[12,13] (Figure 2). Surface nala water from the affected areas is generally free from arsenic contamination, except locally around Kaurikasa village where many dug wells, one pond and a nala are polluted. Arsenic concentration is below 10 ppb in Seonath river near Chowki village where it cuts across the affected belt. Thus arsenic contamination in this area is local and does not have any regional implications[12,13]. Further, the Chhattisgarh basin, located to the east of the rift belt and exposing mid-late Proterozoic platform-type clastic and carbonate sediments (Figure 2) is totally free from arsenic toxicity. Rajnandgaon, Drug and Raipur townships that are located well within the sedimentary basin, although placed on the downstream side of river Seonath, are thus free from the risk of arsenic toxicity[12,13], contrary to such apprehensions voiced by some researchers[10,11].

Arsenic appears to be enriched in acid volcanic rocks and locally in high level granite, possibly by hydrothermal solutions that preferentially permeated conductive host rocks along structurally prepared shear zones[13]. Soil and weathered rock samples from Kaurikasa and other villages exposing acid and basic volcanic rocks often yielded up to 100–250 ppm of arsenic, with common low values in the range of 10–25 ppm of arsenic (GSI unpublished data). Immature soil over weathered rhyolite, porphyritic rhyolite from Kaurikasa area often also yielded up to 500–800 ppm of arsenic. Immature soil and weathered granite from highly polluted Sonsayatola village yielded over 260 ppm total arsenic and about half of it is partitioned in Fe–Mn oxyhydroxide phases[13].

Pyrite occurring locally in metabasalt, rhyolite and quartz reef along some shear zones from the study area, is often arsenic-bearing. But if arsenic is being released to the groundwater mainly by oxidation of pyrite or arsenopyrite at rock–water–air interface, a positive correlation of concentration of arsenic with SO_4 is expected. But no such correlation exists, whereas SO_4 correlates directly with Ca and total dissolved salt (TDS) content both for dug wells and tube wells (Figures 3 and 4). Tube-well water from Kaurikasa, Joratarai, Sonsayatola and water from artesian bore-holes from Gurwandi area (Figure 2) having very high concentration of arsenic (130–2350 μg/l) have very low concentration of SO_4 (3–14 mg/l)[13].

On the other hand, no specific sources of arsenic have been identified for the Bengal Basin, but several potential minor sources occur in the Ganga catchment, both in the Himalayas and in peninsular India. Abundant occurrences of biotite–chlorite, other ferromagnesian minerals and/or their ironhydroxides bearing altered products containing limited concentration of arsenic, and minor occurrences of polymetallic sulfides, especially in the Himalayas can be adequate sources of arsenic for the Ganga delta. Arsenic in solution or sorbed in phases of Fe–Mn-oxyhydroxide as coatings on sediment grain would get preferentially entrapped in argillaceous organic-rich mid-Holocene deltaic sediments. The average value of arsenic concentrations from sand and clay (3.8–4.8 and 9.5–12 ppm, respectively[31]) in the affected aquifer sediments from West Bengal is not found to be unusually high and thus can be accounted for from these lean sources discussed above.

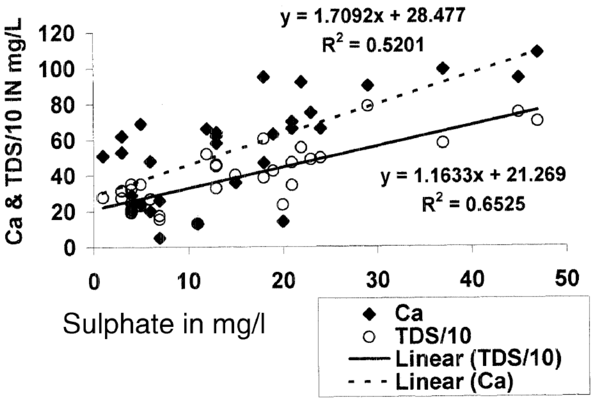

Figure 3. Covariance of sulphate concentration with that of Ca and total dissolved salt from tube-well water in and around Kaurikasa.

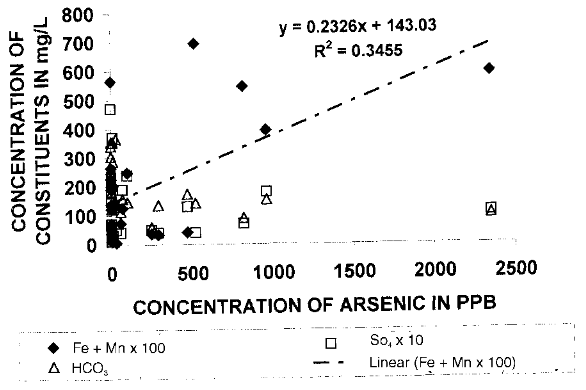

Figure 4. Arsenic concentration showing no relation with that of sulfate or bicarbonate, but weakly correlates with Fe + Mn for tube-well water in and around Kaurikasa, having high arsenic.

Contrary to claims otherwise[1–3,17], our mineralogical studies indicate that arsenic-rich pyrite or separate arsenic minerals are rare or absent in the affected aquifer sediments from West Bengal. However, rare presence of frambroidal pyrite, pyrite in woody peat, as cement-like coating on iron-rich heavy minerals such as Ti-bearing magnetite (Figure 5) is recorded[22–24]. These pyrites are authigenic and biogenic in nature. Very similar mode of occurrences of biogenic pyrite is attributed to activities of sulphur reducing bacteria[19]. In an alluvial aquifer in northwest Mississippi, Fe- and Mn-reducing bacteria that liberated dissolved Fe and Mn, was subsequently precipitated as authigenic siderite, pyrite and rhodochrosite in a zone of sulphate reduction[32]. Organic colony of arsenic-bearing sideritic concretions and framboidal pyrite recorded in aquifer sediments from Ghetugachi area is a closely comparable feature[25,33].

Arsenic content in affected aquifer sediments from four test boreholes of 60 m depth in West Bengal, is neither unusually high nor much different from adjacently occurring uncontaminated aquifers. Fe-rich magnetic fraction of aquifer sediment and parts of feebly magnetic fraction comprising Fe-hydroxide coated clay and detrital grains, Fe–Mn-sideritic concretions, biotite–chlorite are found to be arsenic-enriched[34]. Chemical analytical results indicate that arsenic content of feebly magnetic sediment fraction often has crude positive correlation with percentage of these constituent fractions (Figure 6). Correlation often improves when some of these fractions are considered together[25].

The percentage of Fe-rich magnetic fraction is generally very low in these sediments, but this fraction is most enriched in arsenic (14–112 ppm). Arsenic enrichment in Fe-bearing or Fe-adsorbed mineral grains is attributed to the activities of Fe(III)-reducing bacteria which has to come in contact with solid surface of iron-bearing phase to reduce Fe(III). Recent studies have established that iron-rich groundwater (Fe > 1 mg/l) is also caused due to activities of Fe-reducing bacteria, which preferentially reduces least crystalline Fe–Mn-oxyhydroxide phases. The latter have great capacity specifically for adsorbing or co-precipitating arsenic and other trace elements, which are released to the groundwater on their reductive dissolution and oxidation of co-deposited organic matter[19,35,36]. That reduction of FeOOH is common and intense in the affected aquifers of Bengal basin is shown by high concentration of dissolved iron concentration (9–36 mg/l) from the Ganga delta[21], as against traces or very low concentration of sulphate. Dissolved iron concentration is signi-

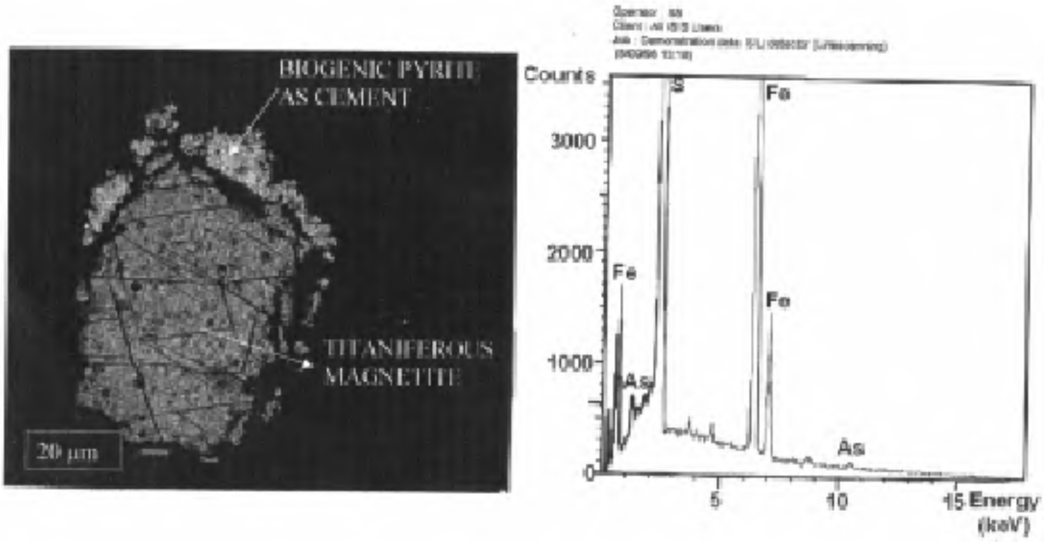

Figure 5. Titaniferous magnetite grain with a cement rim of pyrite in affected aquifer from Ghetugachi area. SEM EDX spot analysis of pyrite indicates its arsenic-bearing nature.

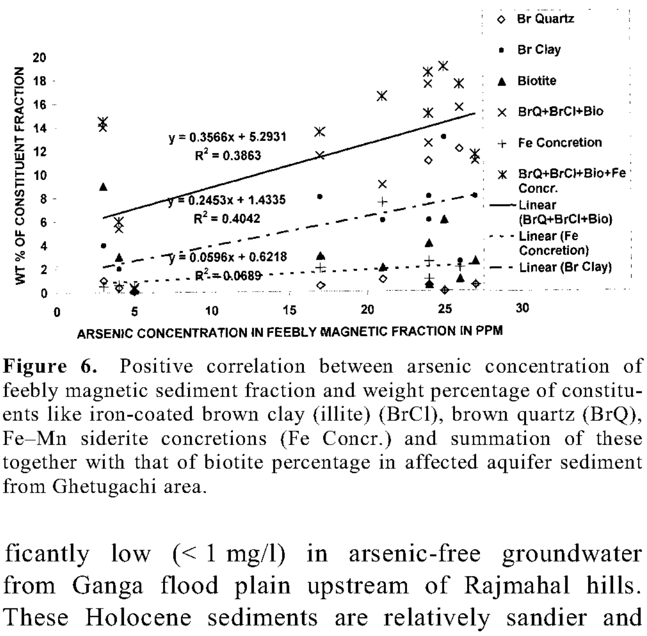

Figure 6. Positive correlation between arsenic concentration of feebly magnetic sediment fraction and weight percentage of constituents like iron-coated brown clay (illite) (BrCl), brown quartz (BrQ), Fe–Mn siderite concretions (Fe Concr.) and summation of these together with that of biotite percentage in affected aquifer sediment from Ghetugachi area.

ficantly low (< 1 mg/l) in arsenic-free groundwater from Ganga flood plain upstream of Rajmahal hills. These Holocene sediments are relatively sandier and less rich in organic matter, which conditioned lower initial retention of arsenic and much lower rate of later release by not developing adequate reducing condition and microbial environment[21–24].

In the arsenic-affected areas of Dongargarh rift belt, Fe concentrations are low in dug wells (0.01–0.3 mg/l) and in most tube wells (0.01–0.5 mg/l), which restricted mobilization of arsenic. There is no correlation between arsenic and iron concentrations (as there are multiple sources of iron), but water from tube wells with high values of arsenic concentration often has high Fe (max 4.86 mg/l) and Mn concentration (Figure 4). HCO_3 in groundwater from the area varies from 61 to 392 mg/l. In this rocky belt, arsenic was mainly released by alteration and weathering of arsenic-enriched acid magmatic rocks of the Dongargarh rift zone. Release of arsenic is insignificant from locally present arsenic-bearing pyrite and arsenopyrite. Arsenic released by decomposition of host rocks might have remained locked and adsorbed in Fe–Mn-oxyhydroxide phases and is mobilized to groundwater by their reductive dissolution only under conducive environment. Thus the geochemical process of release of arsenic to groundwater from parts of Dongargarh rift zone is broadly similar to that of alluvial aquifer of Bengal basin.

Groundwater from the arsenic-affected shallow (< 70 m bgl) aquifers in Bengal basin is isotopically distinct from the arsenic-free deeper (100–200 m bgl) aquifers[37,38]. Rain, river and flood waters are continually recharging the former, whereas the old waters in the latter may not be getting recharged under natural condition. Some samples of groundwater with elevated concentration of arsenic recorded from some deeper wells are found to be isotopically similar to shallow groundwater and thus represent in-puts from shallow aquifer, either through the shallow level screens or due to leakage. Contrary to the inference otherwise[37], the process of enhanced recharging of shallow aquifer, because of extensive groundwater abstraction would enforce movement of groundwater. This would in turn mobilize strongly reducing degraded organic products enriched in groundwater through the FeOOH-bearing sediments, enhancing reduction and release of sorbed arsenic to groundwater[25].

The natural process of release of arsenic to groundwater can also be microbially activated to remove arsenic by inducing precipitation of iron sulphide that would also sorb co-precipitated arsenic and thereby clean the groundwater. *In situ* bio-remediation is an emerging technology that can be a low-cost alternative to standard 'pump-and-treat' processes for cleaning up contaminated groundwater[25,39].

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A precise U–Pb zircon/baddeleyite age for the Jasra igneous complex, Karbi–Analong District, Assam, NE India

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Five Cretaceous alkaline–carbonatite igneous complexes are reported from the Assam–Meghalaya Plateau. These alkaline intrusions have been interpreted to be coeval and associated with the 117–105 Ma Rajmahal–Sylhet flood basalt province. With the existing age information it is possible that this alkaline magmatism may be a late magmatic stage of the Rajmahal–Sylhet large igneous province. Therefore, it is essential to determine high-precision ages for these alkaline complexes in order to understand the detailed temporal evolution and genesis of this basaltic and alkaline magmatism. Out of five igneous complexes, Sung Valley, Swangkre and Samchampi have been dated, but the emplacement ages of the other two, i.e. Jasra and Barpung, are poorly constrained. The present communication reports a new, high-precision U–Pb zircon/baddeleyite age for a differentiated portion of gabbro phase of the Jasra igneous complex.

THE majority of carbonatite occurrences worldwide are associated with alkaline, mafic and ultramafic rocks and

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