

The arsenic quagmire in Bengal aquifers – the missing links

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It is well understood that the evolution of the Earth with its plurality of environmental elements is the resultant product-mix of geological and biological processes coupled together. Any natural environment reflects an interactive dynamics of mineralogy–biology–chemistry. Consequently, with temporal evolution, the milieu tends to change. Aquifers in the deltaic Bengal basin, in eastern India and Bangladesh, offer such a process dynamics. It has been well documented in the literature^{1–5}.

The environmental nanoparticles derived from the critical zone of the Earth system appear to play a key role in the formulation of specific chemistry in the case of natural waterbodies like groundwater⁶. These aqueous nanoparticles (mineral nanoparticles) act as the initial hosts to arsenic in the aquifers of the Bengal basin – later modified by microbial actions in a reducing atmosphere. Arsenic has also been reported from Southeast Asian countries, particularly Thailand, and Chile in South America. However, not much data are available from these occurrences; hence nothing is known about the role of nanoparticles.

In fact, the presence of arsenic in the abandoned meander channels in the deltaic basin of West Bengal (eastern India) was first reported in the early eighties. Later studies⁷ suggested that the above arsenic concentration could have probably emerged from atypical dispersions of marine organic substances. Such a selective and atypical dispersion is, however, difficult to conceive in tidal incursions. Interestingly, our enquiry into space–time dynamics of optimal river channel networks in the mouth of the Ganges (where the river connects the Bay of Bengal) indicates that they may evolve with the intermittent behaviour of punctuated equilibrium⁸, where long periods of stasis are interrupted by bursts of activity. A tidal wave in the Bay of Bengal expressed as a tidal bore in the optimal channel network could easily inundate the coast with the bore reaching tens of kilometres upstream. This has been observed regularly in the Matla River in the coastal region. The Arafura Sea in New Guinea similarly shows periodic inundation on the coast and in the process cre-

ates a bore reaching 15 km upstream causing floods⁹. The transport of marine sediments is thus a significant possibility. And, in the process, the deltaic basin accumulated the nanoparticles carrying arsenic. Alternatively, arsenic could be derived from the Himalayas and the young fold mountain chains^{10–13} exposing the igneous and metamorphic rocks, transported by the river system and distributed in the deltaic basin, probably enriched later on by the incursions of marine sediments. The association of sulphate and strontium noted in the aquifers of Baruipur, West Bengal, just south of Kolkata (~10 km south) presents a significant evidence of invasion of sea water.

However, a review of all the above reports/publications on arsenic reflects a strong emphasis on chemistry in explaining the occurrence. The spread of its tentacles to the groundwater ambience in and around Kolkata, has not been dealt with in detail, except a few press reports. The role of mineral nanoparticles has not been touched upon, though there are ample evidences on arsenic-contaminated aquifers in and around Baruipur. Moreover, there is very little mention of indispensable microbial function on the type and extent of arsenic in the aquifers.

This note is an attempt to bring to the fore, the above missing links in the arsenic scenario. Moreover, the significance of bacterial respiration of arsenate in the environment and its impact on environmental chemistry have not been highlighted in the context.

Discussion

More than a decade ago it was recognized¹⁴ that arsenate adsorbs strongly to a number of common minerals like ferrihydrite, goethite, chlorite and alumina, which constrain its mobility in aquifers, a complicated pH-dependant phenomenon¹⁵.

Since iron is the most abundant transition metal, and oxygen the most abundant element on the Earth, nature produced iron-oxide nanoparticles like nanoferrhydrites in the critical zone of

the Earth which are found to carry elements and compounds in river and groundwater over great distances⁶. Bengal aquifers are no exception.

During the study over the last seven years, it has been observed that arsenic, irrespective of its source, is adsorbed in the nanoparticles of iron oxide, mainly ferrihydrite. The nanoferrhydrites containing adsorbed arsenic are also found in the cleavage planes of chlorite. Such type of occurrences in white mica is reported from arsenic-contaminated groundwater system in Southeast Asia¹⁶.

To understand the contribution that microbes make towards carrying out the reduction of arsenate As (V) in nature is much complicated by several chemical factors. The ability of microbes to reduce arsenate at lower ambient concentrations, particularly when it is associated with the solid rather than the liquid phase, as an adsorbed ion is not completely comprehensible. The mechanisms known include bacterial destruction of sorptive matrix (ferrihydrite), direct reduction of adsorbed arsenate and reduction mediated by low molecular weight electron shuttles produced by bacteria¹⁴. Also when arsenate is reduced to arsenite biochemically, Fe (III), the naturally occurring oxidant can reoxidize As (III) back to As (V)¹⁷ in an aquatic environment. The reduced arsenite As (III) is more toxic and generally more mobile in nature than is arsenate. But As (III) still significantly retains sorptive interaction with nanoferrhydrites and nanogoethites – thereby constraining its mobility in the environment. Interestingly, the binding of arsenite to nanoferrhydrite could be eliminated by the latter's reduction to Fe (II). However, the extent of the ability of microbes to reduce arsenate at lower ambient concentrations, as an adsorbed anion in a nanomineral like ferrihydrite, is not yet clearly understood. More work is needed to unravel the biological mechanisms from the adsorptive chemical phenomena. Cell suspensions (washed) of *Sulfospirillum barnesii*, because it respire both Fe (III) and As (V), reduce both Fe (III) and As (V). The interesting part is that As (III) still maintains a strong capacity for adsorption to the remaining unreacted ferrihydrite and

although there is significant mobilization of arsenite As (III) in the aqueous phase, most of it that is formed, remains with the solid phase. The observation is that the ferrihydrite still has a sorptive capacity for As (III), but does not appear to desorb As (V) from its matrix. This, in a field reality of the aquifer, implies that the quantity of arsenic dissolved in the aqueous medium is uncertain. There is a possibility of arsenic remaining as sorbed grains in ferrihydrites of the aquifer and mobilized. The degree of mobilization of the As (III) product is constrained by the type of minerals present in the system studied. Whether microbes can reduce As (V) while it is attached to the mineral surface or if they attack a nanolayer of aqueous As (V), which is in equilibrium with the As (V) adsorbed onto the surface layer, is not known. On the other hand, Tadanier *et al.*¹⁸ suggest that a microbial reduction of stabilized aggregates of iron oxide with adsorbed As (V) effects a disaggregation of the nanoferrhydrite particles bearing arsenic. As a result, the mobility of arsenic in the groundwater is increased.

The discussion above shows that the question, 'In what form does arsenic occur in the aquifers of the Bengal fluvio-deltaic basin?' is still befuddled with missing links. This presentation, however, points towards the following: (i) It is present as As (III) in solution; (ii) It is present in the water medium as adsorbed As grains in mostly nanoferrhydrites and also in nanogoethites and chlorites (in nanoferrhydrites along the chlorite cleavage planes).

The proportionality of (i) and (ii) is not known and varies with locality. The problem exposes the gaps in our knowledge requiring detailed research which will help seek a permanent solution to the problem. Moreover, the sandy sections of the aquifers are significantly enriched with arsenic. This is because the porosity network in the sandy layers is higher than in other layers. Studies pertaining to transport of nanoparticles in complex natural pore systems within the

sediments also warrant interdisciplinary research.

Bioremediation

If As is not present as adsorbed grains in mineral nanoparticles, the conventional wisdom is that As is sorted to Fe-oxides and is reductively dissolved. There is still a debate about the source of organic matter driving the reduction. It is relevant if one is withdrawing water from a fluvio-deltaic aquifer. Fe-oxide filters worked reasonably well as a low-tech method. It has been tried in many high-rise apartments in the southern part of Kolkata city, but works within its limits.

Assuming that water is reducing with high Fe concentrations, letting the water set so that iron can oxidize and precipitate is another way to reduce As. But there are issues with these methods and bacterial contamination; so disinfection is the key.

Yale University engineers have combined nanopowders (of Al + Ti) and chitosan – derived from crustacean shells to clean water containing As. Preparation of beads from the above mixture is the initial step. The beads which can be reused have promise for the Bengal delta where arsenic is a killer (courtesy Gwyneth Shaw, New Haven Independent @ NH 1 Nanoblog, 13 July 2012).

The enrichment of arsenic in the groundwater below the high-rise buildings in Kolkata is interesting. Is the phenomenon due to an environmental systems collapse^{19,20}?

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ACKNOWLEDGEMENT. We thank Dr M. F. Hochella Jr and Dr Madeline Schreiber, Virginia Tech University, USA for advice.

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