Impact of local recharge on arsenic concentrations in shallow aquifers of Chakdaha, India and Araihazar, Bangladesh

Jerome Métral 1, Laurent Charlet 1, Sara Bureau 1, Sukumar Basu Mallik 2, Sudipta Chakraborty 3, Kazi M. Ahmed 4, M. W. Rahman 4, Zhongqi Cheng 5 and Alexander van Geen 5*

1 Environmental Geochemistry Group, LGIT-OSUG, University of Grenoble, BP 53, F-38041 Grenoble, Cedex 9, France, E-mail: j.me@laposte.net, laurent.charlet@obs.ujf-grenoble.fr

2 Department of Geological Sciences, Jadavpur University, Calcutta, India, E-mail: s_basumallik@yahoo.co.in

3 Department of Chemistry, Kalyani University, West Bengal, India, Email: chakrabortysudipta@hotmail.com

4 Department of Geology, University of Dhaka, Dhaka 1000, Bangladesh

5 Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA, E-mail: avangeen@ldeo.columbia.edu

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*Corresponding author

Phone: +1 845 365 8644

Fax: +1 845 365 8154
Abstract

Background: The origin of the spatial variability of dissolved As concentrations in shallow aquifers of the Bengal Basin is poorly understood. To address the issue, we compare here detailed transects of aquifer solids and groundwater perpendicular to the banks of the Hooghly River in Chakdaha, India, and the Old Brahmaputra River in Araihazar, Bangladesh. Results: Variations in surface geomorphology mapped by coring and electromagnetic conductivity surveys indicate that coarser, relatively permeable surface soils are associated with underlying aquifers that are mildly reducing, characterized by Fe(II)/Fe ratios in acid-leachates of the solid phase <0.6 and concentrations of sulfate in groundwater >5 mg L^{-1} down to a depth of ~20 m. In contrast, finer-grained surface cover is associated with elevated Fe(II)/Fe ratios and very low sulfate concentrations. The patterns suggest that local recharge supplies provides a significant flux of oxidants right at the bank of the Hooghly rivers and at a distance of 500-1500 m from the rivers below regularly flooded and permeable soils. The mildly reducing conditions maintained by such local recharge are associated with generally low As concentrations in both Chakdaha and Araihazar. The more impermeable soils insure a weaker recharge, more reducing conditions, and are associated with higher As concentrations. The patterns of local recharge appear to exert a greater influence on As concentrations in groundwater than the availability of mobilizable As in the solid phase, which is actually considerably higher in Chakdaha (3.1±6.5 mg kg^{-1} P-extractable As, n = 60) than in Araihazar (1.1 ±1.5 mg kg^{-1} P-extractable As, n = 43). Conclusions: The strong influence of local hydrology on aquifer geochemistry documented in this study for two different areas points to the need for integrated investigations at high spatial resolution to unravel the complex mechanisms underlying the widespread enrichment of groundwater with As in shallow aquifers of the Bengal Basin.
1. Introduction

Following the attribution of skin lesions affecting villagers of West Bengal (India) to arsenicosis in the mid 1980’s, studies of the groundwater As problem have been conducted throughout the Bengal Basin across a range of spatial scales. Most of the initial efforts have focused on mapping the extent of the problem by testing the As content of a subset of existing tube wells over large areas at the ~10-100 km scale\(^1,2\) (Fig. 1). This important work demonstrated that some areas were clearly more affected than others at the ~100 km scale, while at the same time indicating significant variability at smaller spatial scales. In parallel, the vertical dimension of the problem began to be addressed by drilling and the purposeful installation of nests of piezometers\(^2\). Variations in the composition of groundwater and aquifer solids for constituents other than As, equivalent to explorations in geochemical space, have also been documented in an attempt to identify the processes responsible for As mobilization\(^2,3,4,5\). The recovery of aquifer material during drilling also led to incubations under a range of conditions that were typically somewhat different from the original conditions in the subsurface\(^6,7\). Despite these multiple approaches and nearly a decade of field and laboratory work conducted by various teams, a broad consensus has yet to emerge with respect to the most basic factors that lead to elevated As concentrations in groundwater of the Bengal Basin. A key issue such as the source of organic carbon that drives Bengal delta aquifers enriched in As towards reduction is still disputed\(^5,8,9\). Moreover, recent work has shed doubt on microbial reduction of Fe oxhydroxides as the only cause of As mobilization\(^10,11\).

In this paper, we argue that variations in aquifer properties on lateral scales of ~100 m must be considered to preserve any hope of understanding the process of As mobilization in relatively shallow (<20 m) aquifers of Holocene age. These are the aquifers tapped by a
majority of existing private wells; groundwater in this depth range also encompasses the widest range of As concentrations\textsuperscript{2}. The primary motivation for this study was the issue of applicability of recent findings from Araihazar, Bangladesh, indicating that interactions between geology and hydrology at the 10-100 m scale regulate As concentrations in shallow aquifers\textsuperscript{12,13,14}, to other regions of the Bengal Basin. We wanted to know, in particular, if the distribution of As in groundwater of Chakdaha, India, could be re-interpreted in terms of variations in local hydrogeology instead of a plume emanating from a “hot spot”\textsuperscript{15,16,17}. The availability of an inexpensive device that builds on the drilling method use to install wells in both West Bengal and Bangladesh\textsuperscript{10} led us to collect new detailed transects of groundwater and aquifer solid properties from similar settings but widely separated portions of the Bengal Basin. We also present here new surface geophysical data to constrain the nature of surface soils in the areas surrounding the two transects. The next two sections describe the main features of the two study areas and the methods used to collect and analyze aquifer material. The main geophysical and geochemical observations are then described with relatively little interpretation. In the subsequent discussion, spatial relationships in the data are examined in the context of a simple conceptual model of groundwater recharge and flow. We then examine some of the systematic relationships between the various geochemical parameters and conclude with some recommendations for future work.

2. Geological Setting

Previous studies have been conducted in the two areas selected for this comparison. Chakdaha block, 65 km to the north of Kolkata, is located in the Ganges River delta floodplain and bordered on the west side by the Hooghly River, the largest tributary of the Ganges in West Bengal, India (Fig. 1). Groundwater pumped from 235 tube wells distributed over a 19 km\textsuperscript{2} area and ranging in depth from 5 to 200 m has been analyzed for As and major
ions in the laboratory. Concentrations of As in roughly half the sampled wells exceed the Indian standard for drinking water of 50 µg L$^{-1}$, with the highest levels (up to 400 µg L$^{-1}$ As) restricted to the 10-40 m depth range. The 1800-m transect of groundwater and sediment properties presented here extends from the bank of the Hooghly River to the rim of the Chakdaha village, where a “hot-spot” in groundwater As at a depth of ~30 m has been documented. A small stream parallel to the Hoogly River passes roughly mid-way through the cultivated fields that separate the village from the river bank (Fig. 2a). The relative elevation of the drill sites was not measured in India, but the appearance of the topography is very flat. The only exception is Chakdaha village at the inland end of the transect, which is elevated by about 2-3 m relative to the adjacent fields.

The setting of the study in Araihazar upazila, Bangladesh, 30 km northeast of Dhaka, is comparable in some ways. A blanket survey of groundwater As has shown that in this region too half the ~6000 wells distributed over a 25 km$^2$ area do not meet the Bangladesh standard for drinking water of 50 µg L$^{-1}$ As, with particularly high levels (up to 800 µg L$^{-1}$) observed in the 10-30 m depth interval. The Old Brahmaputra River passing through the area is considerably smaller than the Hoogly River, however, stops flowing during the dry season and its color suggests elevated dissolved organic carbon concentrations. Supply of fresh sediment to the area is therefore limited today, although there is evidence of a much larger stream, possibly a tributary of the Brahmaputra River, passing through the area a few hundred years ago (Weinman et al., in review). The 450-m transect of groundwater and sediment properties obtained in Araihazar extends from the bank of the Old Brahmaputra River, through Balia Para village, and ends in a low-lying expanse of fields that appears to be a filled river channel (Fig. 2b). The immediate area contains a fairly large (30 by 70 m) rectangular pond located, just east of Balia Para village. The relative elevation of the drill sites in
Bangladesh was measured within ±1 cm using a transparent water tube filled with water extended from one drill site to the next. Here too, the village is elevated ~2 m relative to the adjacent cultivated fields, but is between the river and the fields. Concentrations of As in wells <25 m deep are typically elevated (253±132 µg L⁻¹, n=75) in this particular village 17.

3. Methods

3.1 Surface electromagnetic (EM) conductivity survey

Geophysical surveys of the 2 km² area surrounding the transect in India and the 0.2 km² area surrounding the shorter transect in Bangladesh were conducted using a Geonics® EM31 instrument deployed horizontally20,21,22,23. The instrument measures the interactions between the ground and an electromagnetic field generated by a transmitter coil. In theory, 50% of the signal is generated in the upper 90 cm of the soil; conductivity of layers below 180 cm depth still accounts for 27% of the signal 18,22. Aziz et al. 13 compared EM conductivity measurements over broader area of Araihazar with the properties of soil collected with a hand-auger and concluded that the EM conductivity signal is determined by the clay content of the soil and the concentration of major ions in soil water. In the study by Aziz et al., EM conductivities in the 20 to 40 mS m⁻¹ range were typically observed over clayey soils with an elevated major ion content and <10 mS m⁻¹ over for sandy soils with a low major ion content.

3.2 Water and Sediment Sampling

Unconsolidated deposits were drilled in India and Bangladesh using the manual “hand-flapper” method using sections of PVC or galvanized iron (GI) pipe25,26. A total of 7 boreholes ~250 m apart were drilled to a depth of 30 m along the Indian transect. In Bangladesh, the 5 boreholes are only ~125 m apart and extend to a depth of ~20 m. During
drilling, variations in basic lithology (sand, silt, or clay) were recorded on the basis of the borehole washings. At depth intervals of 2-4 m, the drilling was interrupted to deploy a simple device, the needle-sampler (van Geen et al., 2004), for collecting 104 matched 100 mL slurries of groundwater and sediment from a depth ~0.3 m below the bottom of the drill hole. An additional set of 21 needle-samples was collected only 0.3-1 m deeper than the previously sampled interval. Immediately after collection, the headspace of the needle-sampler was purged with N₂. About 5-10 mL of groundwater contained in the needle-sampler was then filtered under a gentle N₂ pressure through a 0.45 µm syringe filter and into acid-leached polyethylene scintillation vials (Polyseal cap). Another aliquot of groundwater was filtered into scintillation vials that had been rinsed with MQ water only. Sediment contained in the N₂ purged needle-sampler was stored in the dark until further processing on the evening of collection. With the exception of 2 profiles obtained in Bangladesh in January 2003, all samples were collected between March and May 2005. The conductivity of groundwater samples collected in 2005 was measured with a calibrated TetraCon WTW probe on the day of collection. Water from the Hooghly River and the Old Brahmaputra River collected in 2005 was also filtered through a 0.45 µm syringe filter and stored in acid-leached and MQ-rinsed scintillation vials. Surface or well water used for drilling and water overflowing from the drill hole was also sampled and filtered. Finally, groundwater samples were collected from an additional 39 tube wells in India after pumping at a rate of 20–35 L min⁻¹ for at least 5 min.

3.3 Solid phase extractions

Sediment collected with the needle-sampler at 2-4 m intervals was subjected to two types of treatment. The first was a 10% hot HCl extraction that is likely to release by dissolution As bound to amorphous and labile crystalline Fe oxyhydroxides phases as well as, potentially, As
coprecipitated with acid-volatile sulfides. On the evening of sampling, the proportion of Fe(II) and Fe(III) contained in the HCl leach was measured spectrophotometrically with ferrozine. The second extraction takes place over 24 hours and uses a 1 M Na₂HPO₄ (pH = 5) solution, purged with N₂, to dislodge by anion exchange the relatively mobile fraction of As bound to Fe oxhydroxides and, potentially, As bound to adsorbed humic acids.

3.4 Chemical analyses

At least 1-2 days before analysis, groundwater and river samples stored in acid-leached scintillation vials were acidified to 1% HCl (Optima, Fisher Scientific) to ensure re-dissolution of Fe oxhydroxides that might have precipitated. All water samples were diluted 1:10 in 1% HNO₃ (Optima, Fisher Scientific) and analyzed for As, Ca, Fe, K, Mg, Mn, P, Na, and S by high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) at Lamont-Doherty Earth Observatory of Columbia University. The method has a detection limit of ~1 µg L⁻¹ for As and a precision of ~5% for all constituents. Sediment leachates were also analyzed by HR ICP-MS following 1:100 dilution for As and Fe. Water samples stored in scintillation vials that were not acid-leached were analyzed for Cl⁻, Br⁻, F⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻ by ion chromatography (Dionex DX500 and a Dionex separation column). The method has a detection limit ~0.1 mg L⁻¹ and a precision of ~ 10% for all anions. With the exception of one outlier, S determinations by HR ICP-MS and SO₄²⁻ by ion chromatography were essentially identical (see Supplementary Material).

4. Results

4.1 Lithology

The drilling at I.1-I.7 shows that the lithology is quite variable along the 1500 m transect at the Indian floodplain site. Surface clay layers ranging from 1 to 6 m in thickness were
recorded at 5 out of 7 sites (Fig. 3a, c). At sites I.1 and I.5, instead, coarse to fine sand deposits similar to the deeper aquifer material extend all the way to the surface. Even at those sites, however, several clay layers were encountered until drilling stopped at 30 m depth. The aquifer material was always grey in color and occasionally interrupted by 0.3-1 m lenses of fine silt or clay. At the onset of the monsoon in June, the entire low-lying region where the profiles were obtained in India is flooded.

In Bangladesh, the drillers had to work through a 4-10 m thick surface clay layer at all sites before reaching grey aquifer sands (Fig. 3b, d; Note: profiles B.2 and B.4 are identical to profiles NS-7 and NS-8 reported by van Geen et al, 2006 27). Drilling was stopped at all 5 sites when a second thick clay layer was encountered at 18-20 m depth. Clay lenses were not encountered within the sandy aquifers in Bangladesh, with the exception of two intervals at B.1 (Fig. 3). At the onset of the monsoon, only the sites of B.1 and B.5 are typically flooded because sites B2, B3, and B4 are all elevated relative to the open field areas.

### 4.2 Spatial patterns of EM conductivity

Electromagnetic conductivity was measured in India at ~300 locations distributed over a ~2 km² area and ranged from 8 to 63 mS m⁻¹ (average = 31±11 mS m⁻¹). Over half the readings in India exceeded 30 mS m⁻¹ (Fig. 3g). The spatial density of sampling was sufficient to reveal a ~200 m swath of conductivities <20 mS m⁻¹ along the Hooghly River and another pocket of low EM conductivity extending from I.4 to I.5 (Fig. 3a). Drill holes I.1 and I.5, where sandy deposits were observed to extend all the way to the surface, are both located within areas of relatively low EM-conductivity.
The presence of numerous dwellings constructed of corrugated iron plates and overhead power lines limited the collection of EM conductivity data to ~100 readings over a ~0.2 km² area in Bangladesh. The EM measurements span a narrower range of 8-27 mS m⁻¹. The average conductivity (12±4 mS m⁻¹) is also over a factor of two lower than in India, with over half the readings <13 mS m⁻¹ in Bangladesh (Fig. 3h). In contrast to India, EM conductivity values are lowest inland in Bangladesh rather than along the river (Fig. 3b).

4.3 Reproducibility of needle-sampling

True replication is not possible with the needle-sampler because the same depth interval cannot be sampled twice. The risk is perturbation of the groundwater sample, not the sediment. Indeed, deployment of the device within a PVC pipe essentially eliminates the possibility of contamination of the bottom of the hole with sediment material falling from a shallower depth² (van Geen et al., 2004). The drilling procedure requires the hole to be entirely filled with water, which sets up a hydraulic head in the hole that is 1-5 m higher than the water table of the underlying aquifers. Timing is therefore of the essence because hole water will eventually migrate to the depth sampled by the needle. Fortunately, such contamination can typically be detected because hole water is laden with clay particles that remain in suspension. We occasionally observe clay particles in water collected by the needle-sampler and attribute their presence to migration of groundwater below the bottom of the hole or to an early trigger of the sampler. This was confirmed independently by comparing the composition of hole water for relatively unreactive constituents such as the major cations. Of the set of 104 samples collected at 2-4 m interval, only one outlier from I.1 at 19 m depth was eliminated from further consideration because its groundwater composition was similar to that of hole water.
The 21 pairs of samples collected within 0.3-1 m of each other in India and Bangladesh do provide a measure of replication, although it cannot be disentangled from the spatial variability of the composition of groundwater over very short distances. In the case of Ca, Mg and Si concentrations spanning the 10-30 mg L$^{-1}$ range, the correspondence between “replicates” is remarkable, and not merely because the profiles at a particular location are invariant (Fig. 4 and Supplementary Material). The agreement between pairs of samples is somewhat weaker for Na and K, suggesting that water-rock interactions (e.g. micas) result in greater spatial variability for the major monovalent cations (Supplementary Material). The agreement is encouraging also in terms of sulfate and Mn concentrations for the paired samples (Fig. 4), taking into account the likelihood that redox reactions produce a more heterogeneous distribution in the subsurface. Most importantly, there is a good correspondence between As concentrations measured for pairs of samples (Fig. 4). Deviations from the one-to-one correspondence are clustered in the direction that is consistent with the increase in As concentrations with depth that is typically observed in shallow aquifers$^{2,5,18,26,32}$. In contrast to concentrations of the major cations, sulfate, Mn, and As, there is little correspondence between concentrations of Fe for pairs of samples sampled 0.3-1 m apart. We believe this is a reflection of particularly pronounced spatial variability, although a sampling artifact cannot be ruled out with absolute certainty. The syringe filters typically turn light brown, and eventually clog, but we believe this to be due to trapping of fine grained particles rather than Fe precipitation. For constituents other than Fe, there is little doubt that the spatial variability documented with the needle-sampler is real and not a sampling artifact.

4.4 Major cations in river and groundwater

River and ground waters of the Bengal Basin are typically circum-neutral (pH = 7.0±0.5). The combined concentrations (in equivalents) of the major cations Ca, K, Mg, and Na
therefore provide a useful proxy of conductivity and the concentration of total dissolved solids (see Supplementary Material). Because conductivity was not measured in groundwater at sites B.2 and B.4 sampled in January 2003 in Bangladesh, we discuss hereon only the combined concentration of major cations. The concentration of major cations in both the Hooghly and Old Brahmaputra rivers (3 and 4 meq L\(^{-1}\), respectively) is lower than for any of the groundwater that was sampled. In India, the combined concentration of major cations in groundwater is relatively low (<8 meq L\(^{-1}\)) at the site closest to the Hooghly River (I.1) and below the patch of low EM conductivity further inland (I.4 and I.5; Fig. 3a, e). At two of these sites (I.1. and I.5), the thick clay layer recorded at other locations along the same transect is absent. There is also a broad association between surface EM conductivity and major cation concentrations in Bangladesh. Major cation concentrations in groundwater are relatively low (<6 meq L\(^{-1}\)) in the inland region where lower EM conductivities were recorded (Fig. 3b, f). Major cation concentrations are also low in groundwater along the banks of the Old Brahmaputra River at B.1, but rapidly rise to elevated values inland at B.2.

### 4.4 Arsenic in river and groundwater

Concentrations of As in filtered water from both the Hooghly and the Old Brahmaputra rivers are low at 6 µg L\(^{-1}\). The highest groundwater As concentrations in India (~400 µg L\(^{-1}\)) were encountered on the banks of the Hooghly River at I.1 (12 m depth) and about 1500 m inland at I.6 (18 m), the location of the previously identified “hot spot”. In Bangladesh, As concentrations of 500-600 µg L\(^{-1}\) were measured at 12 and 14 m depth in B.2, about 100 m inland of the Old Brahmaputra River. Of the total of 62 intervals sampled 1.5-3 m apart vertically in India and 42 similarly spaced intervals in Bangladesh, essentially the same proportion of groundwater samples contains 50-200 µg L\(^{-1}\) As (44 and 43%, respectively). The two study sites differ at the low and at the high end of As concentrations, however. The
proportion of samples containing <50 µg L⁻¹ and >200 µg L⁻¹ is roughly balanced in India (27 and 29%, respectively), whereas in Bangladesh the number of samples containing <50 µg L⁻¹ As is only one quarter the number containing >200 µg L⁻¹ (12 and 45%, respectively).

There is a striking difference in the depth distributions of As in India and Bangladesh. At all 5 sites in Bangladesh, As concentrations increase steadily with depth starting from a level of 10-90 µg L⁻¹ in the interval sampled closest to the surface (Fig. 5). At B.1, B.3, and B.5 in Bangladesh, the highest As concentration is reached in the last sample that was collected before the deep clay layer was reached. Whereas the shallowest samples from India also all contain <100 µg L⁻¹ As, none of the profiles show a steady increase in As concentrations with depth (Fig. 5). At I.1 and I.7 in particular, As concentrations are highly variable from one sample to the next and throughout the entire depth range. In Bangladesh, the 200 µg L⁻¹ contour of As concentrations delineates what appears to be a single body of contaminated groundwater that extends from below a depth of ~10 m near the river (B.1-B.2) and is restricted to a depth below ~18 m inland at B.5. There is no evidence in the As data from India of a continuous body of groundwater, but instead a jump in concentrations beneath each clay layer or lens at B.2 and B.5, and to a lesser extent, at B.4. One reason for the highly variable vertical profiles of As and other properties could be the presence of numerous clay lenses at depth in India and their rare occurrence in Bangladesh. Possibly because of the 3-fold longer distance between adjacent profiles, there is also considerably less lateral continuity in the distribution of groundwater As concentrations in India (Fig. 6).

4.5 Redox-sensitive constituents of river and groundwater

The distribution of sulfate in India and Bangladesh is nearly the mirror image of the distribution of major cations. Sulfate concentrations are elevated in both the Hooghly and Old
Brahmaputra rivers at 17 and 14 mg L\(^{-1}\), respectively. In groundwater, sulfate concentrations exceed 10 mg L\(^{-1}\) to a depth >20 m only near the Hooghly River (I.1) and further inland at the western of two profiles located within the low EM conductivity area (I.4 and I.5). In both profiles showing elevated sulfate levels, the concentration of major cations is low (Fig.3e, f, 6d, i). The concentrations of sulfate also exceeds 30 mg L\(^{-1}\) in single shallow sample from India (6 m depth at I.4). In Bangladesh as well, concentrations of sulfate >10 mg L\(^{-1}\) are associated with low concentrations of major cations between 10-18 m depth at B.2 and at very shallow depths at B.4 (Fig. 3d, Fig. 6h). Overall, the proportion of samples with sulfate concentrations exceeding 2 mg L\(^{-1}\) is considerably lower in Bangladesh than in India, however (5 out of 39 vs. 36 out of 60 samples analyzed by chromatography, respectively).

Filtered water from both the Hooghly and Old Brahmaputra rivers contains low but detectable levels of Fe (0.05 and 0.36 mg L\(^{-1}\), respectively). The highest concentrations of Fe measured in groundwater were comparable in India (16 mg L\(^{-1}\) for 21-m depth at I.2) and Bangladesh (18 µg L\(^{-1}\) for 6-m depth at B.2). The average concentration of Fe in all groundwater samples from India (1.7±3.2 mg L\(^{-1}\)) is about half the average for Bangladesh (3.9±4.9 mg L\(^{-1}\)), however. There is a broad correspondence between the distribution of major cations and Fe concentrations in groundwater in India, and therefore an inverse relation to the distribution of sulfate. Major cation and Fe concentrations are low (<0.5 mg L\(^{-1}\)) to a depth of 30 m near the Hooghly River (I.1) and underneath the patch of low EM conductivity further inland (I.4-I.5). Conversely, Fe concentrations are generally >5 mg L\(^{-1}\) at I.2-I.3 and I.6-I.7, typically at depths where major cation concentrations are also elevated (Figs. 3, 6). A similar relationship between dissolved Fe and major cation concentrations does not hold in Bangladesh. Although concentrations of major cations and Fe are both elevated at depths shallower than 10 m at B.2,
Fe concentrations are also >5 mg L\(^{-1}\) below 12 m depth at B.7 in groundwater containing <5 meq L\(^{-1}\) in major cations.

### 4.6 Sediment properties

In both India and Bangladesh, leachable Fe(II)/Fe ratios in the sediment span the 0.3-0.9 range. Fe(II)/Fe ratios never drop below 0.2, the value characteristic of older deposits of orange-brown sands associated with As concentrations <10 µg L\(^{-1}\) \(^{26,32}\). The proportion of samples with Fe(II)/Fe <0.5 is considerably larger in India (23 out of 62 samples) than in Bangladesh (2 out of 42), suggesting a generally less reducing environment in India. Lower leachable Fe(II)/Fe ratios are concentrated in India next to the large and typically rapidly flowing Hooghly River (I.1), within the patch of low surface EM conductivity I.4, and towards Chakdaha village (Fig. 6, i). These are precisely the three areas where low major cations and generally elevated sulfate concentrations are observed. Below the core of the patch of elevated EM conductivity at I.5, both low sulfate concentrations and elevated Fe(II)/Fe ratios indicate more strongly reducing conditions. In contrast to India, elevated Fe(II)/Fe ratios and low sulfate concentrations indicate particularly reducing conditions on the banks of the small and often stagnant Old Brahmaputra River (B.1). A core of more mildly reducing conditions indicated by low Fe(II)/Fe ratios and a few samples elevated in sulfate is located at mid-depth (10-15 m) and some distance away from the Old Brahmaputra River at B.2-B.3 (Fig. 6h, j).

The full range of HCl-extractable As concentrations in the sediment is comparable in India (1-35 mg kg\(^{-1}\)) and Bangladesh (1-19 mg kg\(^{-1}\)). But whereas HCl-extractable As concentrations in 6 out of 62 samples exceed 10 mg kg\(^{-1}\) in India, this is the case for only 1 out of 22 samples in Bangladesh. There is a very broad relationship between HCl and P-extractable As
concentration in both India and Bangladesh (Fig. 7a, b). In the most enriched samples, collected from the eastern end of the transect in India (I.7), concentrations of As in the P- and HCl-extractable fractions are comparable. At the low end of the spectrum, however, concentrations of As in the P-extractable fraction are up to an order of magnitude lower than in the fraction more aggressively separated with hot HCl. Because no HCl-extractable As data are available for 2 out of 5 profiles in Bangladesh, the discussion hereon focuses on the P-extractable As fraction.

Spatially, the highest concentrations of P-extractable As are clustered in the eastern portion of the transect from India, with an average of $11_{-14}^{+14}$ mg kg$^{-1}$ (n = 9) over the entire depth range of I.7 (see Fig. X in Supplementary Material). Concentrations of P-extractable As $>5$ mg kg$^{-1}$ are also observed in 2 samples below 15 m depth at both I.4 and I.5 (Fig. 7a, b). In Bangladesh, only the profile in the middle of the transect (B.3) indicates consistently elevated concentrations of P-extractable As.

5. Discussion

5.1 Inferred patterns of groundwater recharge

In this section, we relate high-resolution geophysical and geochemical observations other than As form both India and Bangladesh to a simple conceptual model of groundwater flow. The model is derived from detailed surveys of surface lithology and EM conductivity, as well as profiles of groundwater age based on the $^3$H-$^3$He dating technique, across an area of Araihazar that is $\sim$100 times larger than the area of the present study$^{12,13,14}$. A key conclusion from these studies is that local recharge is enhanced by an order of magnitude in areas where sandy deposits extend to the surface compared to areas where shallow aquifers are capped with less-permeable silts and clay. Related studies in the same area have shown that locally enhanced
recharge also often prevents the shallowest aquifers from becoming very reducing (i.e., Fe(II)/Fe ratios remain <0.5) in those areas where sandy deposits extend to the surface\textsuperscript{26,27}. The implication is that, at least in Araihazar, local recharge supplies an excess of electron acceptors over electron donors, presumably in the form of oxygen and nitrate. This observation runs counter to the previous claim that recharge might lead to more reducing conditions at depth because of an excess of electron donors in the form of reactive organic carbon\textsuperscript{5}.

The simplest explanation for the combination of low EM conductivity, coarse grain-size of surface soils, low cation concentrations, and elevated sulfate levels observed on the bank of the Hooghly River at I.1 is recharge with river water. Low leachable Fe(II)/Fe ratios 0.5±0.06 to 30 m depth at I.1 compared to the next profile further inland (I.2: 0.68±0.09) indicates that recharge along the river bank prevents the sediment from becoming very reducing. If river water containing 14 mg L\textsuperscript{-1} sulfate in May 2005 is representative of the initial composition of recharge water, then groundwater sulfate levels averaging 13±3 mg L\textsuperscript{-1} to 30 m depth at I.1 indicate that the extent of sulfate reduction is limited within a short distance of the river. Only mildly reducing conditions are confirmed by Fe concentrations <0.1 mg L\textsuperscript{-1} in most samples at I.1. Concentrations of Mn >0.1 mg L\textsuperscript{-1}, at least 5 times higher than in filtered Hooghly River water, indicate however that anoxia is reached by the time presumably oxic river water reaches I.1. At the same time, the presence of 0.3-2 mg L\textsuperscript{-1} NO\textsubscript{3}\textsuperscript{-} in 4 out of 8 samples at I.1 indicates a supply of oxidants other than sulfate when the samples were collected (Supplementary Material). The geochemical profiles suggest that recharge occurs primarily vertically rather than laterally, even at the river bank.
Further inland in India, the relation between enhanced recharge and redox conditions in underlying aquifers appears to be somewhat shifted spatially. Whereas sandy deposits extend to the surface at I.5 and not at I.4, the latter profile is actually located closer to the area where the lowest EM conductivities were measured (Fig. 3). Cation concentrations are relatively low in shallow aquifers at both I.4 and I.5, but leachable Fe(II)/Fe ratios and sulfate concentrations indicate mildly reducing conditions in the subsurface at I.4 only (0.46±0.07 and 14±8 mg L⁻¹, respectively). In fact, Fe(II)/Fe ratios are particularly high (0.75±0.13) and sulfate levels are particularly low (3.17±3.24 mg L⁻¹) at I.5. The observations suggest that although surface deposits recovered during drilling are more permeable at I.5, the expression of enhanced recharge with associated with an excess of electron acceptors is restricted largely to profile I.4. This may be because I.4 is actually closer to the core of the low EM conductivity zone, suggesting that the permeability of the surrounding area may be higher than at I.5. Another possibility is that the shift in the signature of recharge from I.5 to I.4 is caused by a flow of recharged groundwater towards the west during the dry season when the water level of the Hooghly River is below the groundwater level in the floodplain area 15.

In Bangladesh, the Old Brahmaputra River does not have the same impact on the redox state of the closest shallow aquifers as the Hooghly River. The concentration of major cations is relatively low at B.1, but elevated leachable Fe(II)/Fe ratios (0.8±0.14), low sulfate levels (0.5±0.4 mg L⁻¹), and elevated Fe concentrations (5.2±1.2 mg L⁻¹) indicate fairly pronounced reducing conditions. The different impact on groundwater along the riverbank compared to the Hooghly River may reflect stagnant conditions in the Old Brahmaputra River and possibly an excess in electron donors because of a low oxygen content and/or elevated dissolved organic concentrations. Further inland along the transect Bangladesh, however, recharge appears to be associated with an excess of oxidants even if sandy deposits extending to the
surface were not observed at the drill sites. Cation concentrations are low throughout the
depth range of B.4 (3.3±1.4 meq L⁻¹) and sulfate levels are elevated in the shallowest intervals
of the same profile. Leachable Fe(II)/Fe ratios are relatively low at B.4, and mildly reducing
conditions appear to extend at mid-depth (10-15 m) to B.2 and B.3 towards the Old
Brahmaputra River. Elevated sulfate concentrations are occasionally also observed at mid-
depth at B.2. Considered as a whole, the observations suggest that the large pond situated
between B.4 and B.5, or possibly seasonal flooding of the entire low-lying area east of Balia
Para village, results in significant recharge that prevents aquifers from becoming very
reducing along a flow path that extends westward from B.4 at 10-15 m depth. Although B.5
is located just east of this pond, the increase in Fe(II)/Fe ratios with depth at B.5 as well as
elevated dissolved Fe concentrations also suggest a westward direction of groundwater flow.
Even more so than in Chakdaha, groundwater recharge occurring inland appears to be more
important than recharge at the river in Araihazar.

5.2 Comparison of geochemical relationships in India and Bangladesh

It is generally believed that As concentrations in shallow groundwater are regulated by
adsorption onto reactive mineral surfaces rather than solubility with respect to a pure solid.
Detailed spectroscopic investigations of aquifer material collected throughout the Bengal
Basin indicate the presence of As in wide range of minerals, including micas, oxides, and
sulfides, without any obvious association of a particular phase (or lack thereof) with elevated
concentrations in groundwater²,³⁵. Several studies have noted a significant correlation
between the As and Fe content of aquifer particles, as well as an increase in concentrations of
both with decreasing grain-size²,³. In a broad sense, it has also been shown that the As
content of aquifer particles is lower in deeper strata that are typically associated with low As
levels in groundwater²,⁵,³²,³⁵. To the best of our knowledge, however, sampling limitations
have prevented a systematic comparison of groundwater As concentrations in relatively shallow aquifers of the Bengal Basin with sediment properties from precisely the same horizon.

Even though the needle-sampler collects particles and groundwater from the same horizon, there still is remarkably little correspondence between the concentration of As in groundwater and the solid concentration of P-extractable As in India. Indeed, some of the highest As levels in the solid phase at I.5 and I.7 are associated with groundwater containing <100 µg L\(^{-1}\) As and the three intervals containing >350 µg L\(^{-1}\) As all contain sediment with <5 mg kg\(^{-1}\) P-extractable As (Fig. 7c). The situation is somewhat different in Bangladesh, where an increase in groundwater As concentrations is associated with some higher P-extractable As levels\(^{27}\) (Fig. 7d). Unlike the situation in India, the relationship observed in Bangladesh is suggestive of exchange and equilibration As between the solid and dissolved phase.

Why is the association between P-extractable As and groundwater As concentrations stronger in Bangladesh than in India, given that the environments are broadly similar? The geochemical spectrum spanned by the composition of aquifer material in the study areas differs in one major way. The high proportion of sediment samples in India with a leachable Fe(II)/Fe ratio <0.5 and elevated sulfate concentrations, combined with dissolved Fe concentrations <0.1 mg L\(^{-1}\) at I.1, I.4, and I.5 suggest the presence of Fe(III) adsorption sites for a sizeable subset of samples. More reducing conditions and low sulfate levels combined with generally elevated dissolved Fe concentrations in Bangladesh suggest instead a predominance of Fe(II) adsorption sites, in the form of oxyhydroxides\(^{26,36}\) (e.g. magnetite) or possibly sulfides\(^{37,38,39}\) (e.g. mackinawite). We postulate that the proportion of groundwater samples containing <50 µg L\(^{-1}\) As is considerably higher in India than in Bangladesh despite
higher P-extractable As levels because of the particularly high affinity of As for Fe(III) oxyhydroxides compared to Fe(II) oxyhydroxides or sulfides. The lack of strongly adsorbing Fe(III) oxyhydroxides in Bangladesh, and consequently perhaps more uniform adsorption properties for the remaining phases, could explain both why there are fewer samples containing <50 µg L⁻¹ As and why dissolved As concentration broadly increase with the concentration of P-extractable As in the solid phase.

There is growing concern about elevated levels of Mn observed in many wells of the Bengal Basin. Dissolved Mn was recently identified as a confounding variable when measuring the impact of As in drinking groundwater on the mental development of children. Increasing attention is therefore likely to be paid in the coming years to the high proportion of wells in Bangladesh exceeding the WHO guideline for Mn in drinking water of 0.4 mg L⁻¹. Whereas Mn concentrations occasionally exceed 2 mg L⁻¹ only in Bangladesh, the majority of samples at both locations do not meet the current WHO guideline, including most samples containing elevated sulfate levels (Fig. 8). The data confirm that only mildly reducing conditions lead to mobilization of Mn, which helps explain why there is no systematic relation between As and Mn levels in shallow groundwater.

5.3. Impact of recharge on As in shallow aquifers

Precipitation and river water contain little dissolved As and are likely to be associated with an excess of electron acceptors. Either dilution or stronger adsorption could therefore in principle maintain relatively low As concentrations in shallow aquifers where local recharge is strong. The observations in Chakdaha and Araihazar do not systematically fit this simple picture, however, perhaps because both mechanisms play a role and cannot be distinguished in the present study. On the banks of the Old Brahmaputra River, the presence of As at
elevated concentrations in shallow groundwater is not surprising given the indications of strongly reducing conditions from elevated dissolved Fe concentrations, low sulfate concentrations, and elevated Fe(II)/Fe ratios in the solid phase. It is more difficult, however, to explain elevated As concentrations observed on the banks of the Hooghly River in aquifers associated with little dissolved Fe, high concentrations of sulfate, and low Fe(II)/Fe ratios in the solid phase.

Groundwater As concentrations appear to be more systematically suppressed further inland in those areas where recharge is inferred to be significant. With the exception of a few intervals, a plume of groundwater that is low in As concentrations appears to originate from the surface at I.4 and I.5, within the area of low EM conductivity, and dips west to a depth of ~25 m at I.3. The distribution of As in Araihazar associated with other groundwater properties also suggests recharge in the low EM conductivity area surrounding B.4 and B.5 and, though less clearly than in Chakdaha, possibly also westward flow towards the river. Surficial clay layers at B.4 and B.5 at the surface indicates that the recharge area itself was not drilled, even if the impact of recharge was detected in the underlying aquifers.

5.4 Implications for future groundwater As studies

On the basis of an unusually dense array of matched samples of groundwater and aquifer solids from two different study areas, the present study shows that the distribution of As in shallow groundwater of the Bengal delta is likely to be determined by multiple and possibly interrelated processes. Recharge appears to play an important role both through dilution with As-depleted water and an associated excess of electron acceptors. These findings suggest that a new approach may be needed to understand the root cause(s) of As mobilization in shallow Bengal delta aquifers and, by extension, possibly also in other Southeast Asian river deltas.
Past field investigations have given different weight to the relative importance of various geological, hydrological, geochemical, microbial factors. This is the natural reflection of the different spectrum of skills mastered by individual teams and various financial and geographical constraints. Probably by circumstance rather than by design, some areas of investigation such as organic and sulfur geochemistry have been largely overlooked. To overcome these limitations, and by analogy to large projects in high-energy physics, a large international team of scientists should be assembled to study the groundwater As problem at a limited number of carefully selected sites and for an extended period. It would be essential to involve in such studies some of the handful of laboratories with the capacity to measure $^3$H-$^3$He ages. A strong argument could be made for non-traditional funding of such an effort on the basis of the human suffering that could be avoided by mitigating of this vast problem on the basis of sound science.

6. Conclusions

The detailed sections of needle-sampler profiles from India and Bangladesh presented in this study demonstrate that a sampling resolution of ~3 m vertically and ~100 m laterally is necessary to capture spatial variations in a suite of important groundwater and aquifer solid properties. Despite different sampling resolutions in India and Bangladesh, it appears that similar processes control the general distribution of As. The results are not inconsistent with Fe oxyhydroxide reduction as a significant source of As mobilization, but also suggest significant regulation of As concentrations in shallow aquifers of the Bengal delta by recharge and groundwater circulation. This study could not determine to what extent dilution vs. the maintenance of mildly reducing conditions by recharge play a more important in terms of limiting groundwater As concentrations in shallow aquifers. The limitations of this study in terms of generalizable mechanisms suggest that the detailed views of the subsurface afforded
by the needle-sampler needs to be systematically supplemented with measurements of groundwater age.

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Figure captions

Figure 1
Map of the entire Bengal Basin showing the general distribution of As in tubewells
Adapted from Charlet and Polya 2006). based on data collected by Dr. Chakraborti’s
laboratory at the School of Environmental Studies, Jadavpur University, Kolkata, India. Areas
colored in red indicate predominantly unsafe wells, orange a in orange orange areas, and
green predominantly wells containing less that 50 µg L⁻¹ As. Adapted from Charlet and Polya
(Elements 2, 91-96, 2006).

Figure 2
IKONOS satellite images of study areas in India (a) and Bangladesh (b) acquired in April
2000 and November 2000, respectively. The images were processed to emphasize in purple
the water contained in streams, ponds, and irrigated rice paddies. Also shown are symbols
indicating the position of the needle-sampler profile obtained in both areas.

Figure 3
Map of the study areas in (a) Chakdaha, India and (b) Araihazar, Bangladesh showing
distribution of EM (filled squares represent the locations of sampling tubewells; symbols for
needle-sampler profiles are same as in Fig. 2). (c) & (d) Vertical lithological cross-sections in
India and Bangladesh, respectively (black-clay/silt; white-sand). (e) & (f) The distributions of
major aqueous cationic concentrations in India and Bangladesh, respectively. (g) & (h)
histograms showing the distributions of EM in India and Bangladesh, respectively.

Figure 4
Comparison of composition of 21 “replicate” needle-samples collected sequentially 1-3 ft apart in India and Bangladesh. Symbols are the same as for the profiles shown in Figure 2.

**Figure 5**
Vertical profiles of groundwater As concentration in (a) India, (b) Bangladesh. Symbols within the same profile are not connected if two samples were separated by an impermeable clay lens. Symbols are the same as for the profiles shown in Figure 2.

**Figure 6**
The distribution of groundwater As concentrations ([As] \(_T\) = 0-50 µg L\(^{-1}\) (green); [As] \(_T\) = 50-200 µg L\(^{-1}\) (red); [As] \(_T\) >200 µg L\(^{-1}\) (black) in shallow wells plotted in IKONOS imagery map of the study areas in (a) Chakdaha, India and (b) Araihazar, Bangladesh. The contour maps of dissolved As (µg L\(^{-1}\)) (c & d), dissolved Fe (mg L\(^{-1}\)) (e & f), dissolved SO\(_4\)\(^{2-}\) (g & h) and the proportions of Fe(II) in the the acid-leachable Fe fraction of the solid phase (i & j) of the study areas in India and Bangladesh respectively.

**Figure 7**
Comparison of P-extractable As with the acid-leachable As content of the sediment collected by the needle sampler from (a) India, (b) Bangladesh. Correlation between P-extractable As content of the sediment and the groundwater As concentrations for the same set of samples. The symbols used are same as for the profiles shown in Fig. 2.

**Figure 8**
Scatter-plot comparing of sediment Fe(II)/Fe, dissolved Fe, and dissolved Mn as a function of dissolved sulphate for needle-sampler samples collected in India (left) and Bangladesh (right).
The symbols are color-coded within three ranges according to groundwater As concentrations. Dashed lines show the sulfate concentration in the Hooghly and Old Brahmaputra rivers.
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