

## Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications.

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### ABSTRACT

In order to investigate the mechanism of arsenic release to anoxic ground water in alluvial aquifers, we sampled ground waters from three piezometer nests, 79 shallow (< 45m) wells, and 6 deep (> 80m) wells, in an area 750 m by 450 m, just north of Barasat, near Kolkata (Calcutta), in southern West Bengal. High concentrations of arsenic (200 - 1180  $\mu\text{g l}^{-1}$ ) are accompanied by high concentrations of iron (3 - 13.7  $\text{mg l}^{-1}$ ) and phosphate (1 - 6.5  $\text{mg l}^{-1}$ ). Ground water that is rich in manganese (1 - 5.3  $\text{mg l}^{-1}$ ) contains < 50  $\mu\text{g l}^{-1}$  of arsenic. The composition of shallow ground water varies at the 100m-scale laterally and the metre-scale vertically, with vertical gradients in arsenic concentration reaching 200  $\mu\text{g l}^{-1} \text{m}^{-1}$ . The arsenic is supplied by reductive dissolution of FeOOH and release of the sorbed arsenic to solution. The process is driven by natural organic matter in peaty strata both within the aquifer sands and in the overlying confining unit. In well waters, thermo-tolerant coliforms, a proxy for faecal contamination, are not present in high numbers (< 10 cfu/100 ml in 85% of wells) showing that faecally-derived organic matter does not enter the aquifer, does not drive reduction of FeOOH, and so does not release arsenic to ground water.

Arsenic concentrations are high ( $\gg 50 \mu\text{g l}^{-1}$ ) where reduction of FeOOH oxide is complete and its entire load of sorbed arsenic is released to solution, at which point the aquifer sediments become grey in colour as FeOOH vanishes. Where reduction incomplete, the sediments are brown in colour and resorption of arsenic to residual FeOOH keeps arsenic concentrations below 10  $\mu\text{g l}^{-1}$  in the presence of dissolved iron. Sorbed arsenic released by reduction of manganese oxides does not release arsenic to ground water because the arsenic resorbs to FeOOH. Arsenic pollution of ground water is common in the alluvial aquifers of the Bengal Basin because Himalayan erosion supplies immature sediments, with low surface-loadings of FeOOH on mineral grains, to a depositional environment that is rich in organic matter so that complete reduction of FeOOH is common.

*Keywords:* As, arsenic, well, ground water, Bengal Basin, West Bengal, pollution; contamination

## 1. INTRODUCTION

In the Ganges Plain, some 25% of wells that tap ground waters from alluvial aquifers contain high ( $> 50 \mu\text{g l}^{-1}$ ) concentrations of arsenic, the consumption of which threatens the health of millions of people (*e.g.* Chatterjee *et al.* 1995; Chakraborti *et al.* 2002): by, for example, inducing cancers that may prove fatal (Smith *et al.* 2001; Yu *et al.* 2003). One model for the release of arsenic to ground water, *viz.* reduction of sedimentary iron oxides (FeOOH without mineralogical connotations hereinafter) and release of the sorbed arsenic, was outlined by Gulens *et al.* (1979), adopted by Matisoff *et al.* (1982), and systematised by Korte and Fernando (1991). The process is driven by microbial reduction of organic matter (Nealson, 1997; Lovley, 1997; Banfield *et al.*, 1998; Cummings *et al.* 1999; Chapelle, 2000; Lovley and Anderson, 2000). This mechanism was used by Nickson *et al.* (1998, 2000) to explain the occurrence of high concentrations of arsenic in aquifers in the Ganges Plain: it was further developed by McArthur *et al.* (2001) and Ravenscroft *et al.* (2001), who proposed that organic carbon in buried peat was the driver of microbial reduction of FeOOH in the sediments, and that human organic waste in latrines might also locally contribute to arsenic release by providing point-sources of organic matter to enhance local reduction of FeOOH (thereby confusing regional trends of arsenic distribution by adding local signals). These authors also discussed, and dismissed, other mechanisms proposed to explain the pollution of ground water by arsenic, such as oxidation of sedimentary pyrite, and competitive anion exchange of sorbed arsenic with inorganic phosphate from fertiliser; they thereby broke the putative link between the development of irrigation with ground water and the presence of arsenic pollution in ground water.

Although the iron-reduction model is now widely accepted as valid for the Ganges Plain (Bandyopadhyay 2002, Dowling *et al.* 2002; Harvey *et al.* 2002; Anawar *et al.* 2003; Tareq *et al.* 2003), the suggestion of McArthur *et al.* (2001) and Ravenscroft *et al.* (2001) that reduction is driven by buried peat has been disputed. For example, Pal *et al.* (2002) found peat in an arsenic-free area, but did not find it in an arsenic-polluted area nearby. Harvey *et al.* (2002) suggest that reduction of FeOOH is driven by surface organic matter, from river beds, ponds, and soils, that is drawn into the aquifer by irrigation drawdown: this model seeks to re-link irrigation and arsenic pollution of ground water. Should such a linking lead to renewed calls to curb or ban irrigation with ground water, the livelihoods of the rural poor will be affected adversely.

To better define the source of the organic matter driving reduction of FeOOH in the Ganges Plain and to further examine the behaviour of arsenic and iron in ground water, we installed three piezometer nests in a shallow ( $< 45\text{m}$  depth) aquifer near Barasat, in West Bengal (Fig. 1); measured vertical profiles of water composition in them; and took cores for study from the piezometer sites. One piezometer was sited where arsenic poisoning of wells did not occur (site DP), one was where it was thought to be minor (site AP), and one where it was severe (site FP): the sites are less than 350 m apart (Fig. 1). We also sampled wells tapping the shallow ( $< 45\text{m}$ ) and deep ( $> 70\text{m}$ ) aquifers in the area in order to ascertain the lateral extent, and degree, of arsenic pollution. The content of thermotolerant coliform (TTC) bacteria in wells and surface ponds was measured in order to assess their content of faecally-derived micro-organisms, the presence of which indicates the influence of human and animal organic waste. In order to investigate whether the wells changed their composition with time, they were analysed (TTC apart) on three occasions in two years. The results of these studies are presented here.

## 2. LOCATION OF AREA

The study area is located at 22° 44.43' N, 88° 29.45' E (Indian/Bangladesh datum) in the contiguous villages of Joypur, Ardivok and Moyna (JAM hereinafter; Fig. 1) in southern West Bengal. The area is just north of the town of Barasat, Barasat-1 Block, 24 Parganas (North) District, some 20 km north-north-east of Calcutta. The climate of the area is tropical monsoonal with a dry season lasting from December to May. The Hugli River flows from north to south some 13 km to the west of the area, and the Sunti River (mostly dry) runs north-south 1.2 km to the east, joining the east-west draining Sunti Channel

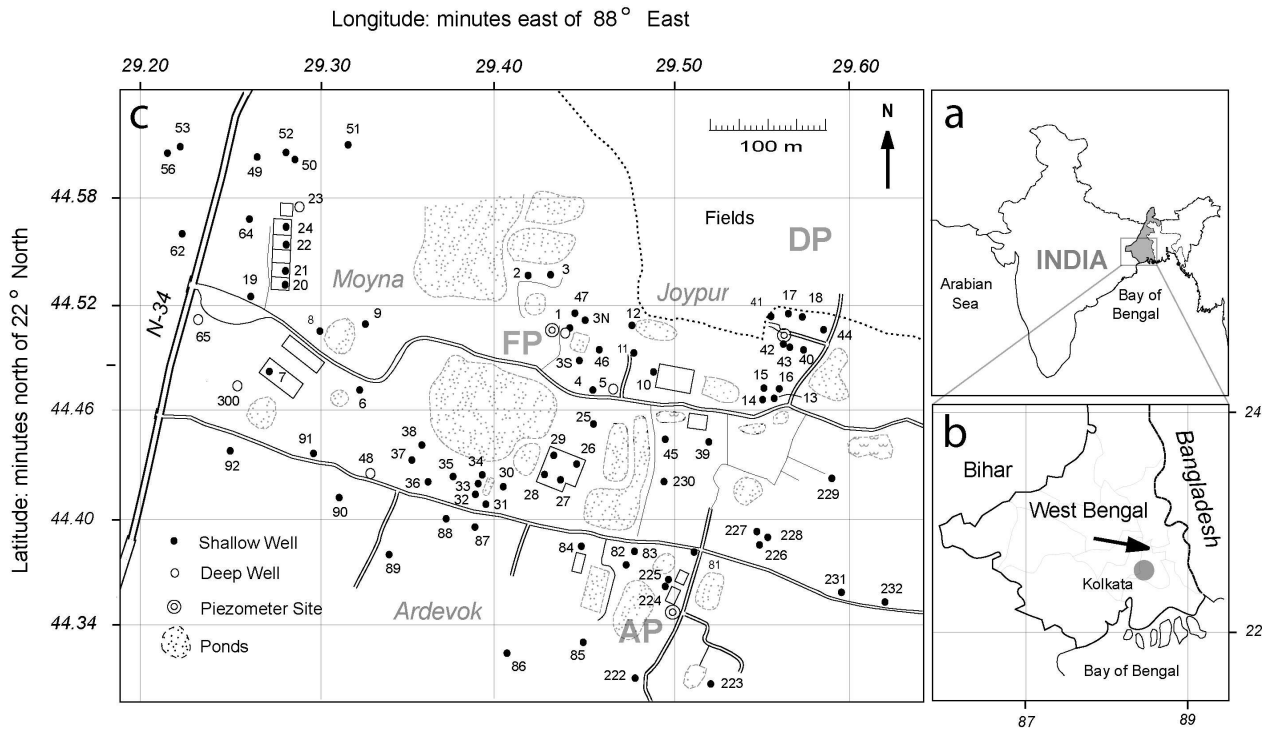


Fig. 1. Location of wells and piezometers in the study area on the northern outskirts of Barasat town, West Bengal. Waved areas are ponds and rectangles represent some of the larger houses. Piezometer sites are double circles at AP, FP, DP. Arrowpoint in b) shows field area. Roads in C are double lines, prominent tracks are single lines. Unfilled circles are deep wells (> 70 m depth), filled circles are shallow wells (< 45m depth). N-34 is national highway 34.

(also dry most months) at Mirathi, about 4 km to the north of the area. The area looks flat but has a regional slope to the north and east; *i.e.* towards the rivers. Superimposed on this is a microtopography that influences local hydrology: relative relief of 2-3 metres exists where major roads are raised above ground level, and where ponds, perched above the local water table by several metres, have dry-season water levels up to 3 m below ground level. These numerous ponds range in size from < 10 m diameter to around 100 m diameter, and are excavated to a depth that preserves natural sealing by the lower part of an aquitard that overlies the shallow aquifer.

## 3. METHODS

Piezometers consist of multiple, independent, wells drilled to different depths and spaced no more than 2 metres apart. They were drilled using the reverse-circulation, hand-percussion, method (Ali, 2003). Using this method, mud and clay samples are recovered with undisturbed cores. In sands, the samples are disturbed. Separately at site AP (Fig. 1), percussive piston-sampling into plastic core-tubes was alternated with rotary wash-boring. The coring gave good recovery from precisely-known depths in all strata. Cores were stored at room temperature until sampled for analysis, as the local groundwater temperature is 25° C. A LECO C/S 125 Analyser was used to analysed the < 0.5 mm fraction of sediments for total sulphur (TS), total carbon (TC),

and total organic carbon (TOC), the last after leaching samples with 10% v/v hydrochloric acid. The difference between TC and TOC is reported as a percentage of calcite. To obtain values of  $\delta^{13}\text{C}$  for calcite, samples were analysed with a Prism<sup>®</sup> mass spectrometer using a common acid bath and NBS 19, a carbonate reference material supplied by the National Bureau of Standards (now National Institute of Standards Technology).

Ground waters were sampled, after purging, from hand-pumped domestic and public wells, in February 2002, November 2002, and March 2003. The depth of each well was recorded at the time of sampling by asking the owner how many pipes were used to install it: commonly, individuals buy 20-foot lengths of pipe and employ a driller to install them. The depths of some wells are uncertain because of a change of owner, or some other circumstance. Water samples drawn from wells were not filtered: an accurate measurement was sought of the amount of arsenic in water consumed by well-users, who do not filter their water. All samples were crystal clear, *i.e.* without visible turbidity. Piezometers fitted with 1.8 m screens were installed in March 2003 in eastern JAM where arsenic poisoning was absent (DP); in south-eastern JAM where it was believed to be minor (AP); and in northwestern JAM where it was severe (FP, Fig. 1). The level above ground of each well in each piezometer nest, relative to an arbitrary level, was established by theodolite survey. Water levels were measured in order to establish hydraulic heads and the direction of ground-water flow. After extensive purging, piezometers were sampled *via* hand-pumps between 5 and 10 days after installation. Piezometer samples were filtered through 0.45  $\mu\text{m}$  membrane filters. All samples for cation analysis were acidified to pH 2 with nitric acid. Samples taken for anion analysis and for stable isotope analysis were not acidified.

Ammonium and nitrate were determined within 2 weeks of collection, and mostly much sooner. Measurements of conductivity, and temperature were made at the well head. Measurements of dissolved oxygen are not given as they are devalued by pump aeration. For piezometers and some wells, alkalinity was measured in the field by pH-titration with sulphuric acid and is reported as bicarbonate: for wells where this was not done, bicarbonate has been estimated by difference of charge balance. No well-sample contained hydrogen sulphide that was detectable by smell after acidification of the sample with sulphuric acid and agitation. Analysis of waters for cations, total-sulphur (reported as sulphate) and total-phosphorus (reported as phosphate) was by ICP-AES and analysis for anions and ammonium was by ion chromatography (including duplicate analysis for sulphate). As a check on ICP determinations of phosphorus, orthophosphate was also determined spectrophotometrically using the molybdenum-blue method. Concentrations of arsenic were measured on acidified samples using graphite-furnace AAS. In order to assess particulate contributions to the dissolved load of well water, the concentration of aluminium in waters was measured and the turbidity of samples was recorded at collection. All samples were crystal clear, *i.e.* without visible turbidity, and concentrations of aluminium were  $< 0.1 \text{ mg l}^{-1}$ , so we assume that our analysis is unaffected by particulate contributions. Measurement of  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) was done with a Micromass Multiflow<sup>®</sup> preparation system on-line to an IsoPrime<sup>®</sup> mass spectrometer. After helium flushing of samples, and addition of orthophosphoric acid, the isotopic composition of carbon dioxide was measured after equilibration for 9 hours at 30°C. Drift corrections were made using a reference-gas pulse that bracketed each sample. Reference materials used were an in-house carbonate and NBS-19. Every third sample was accompanied by a standard, which was used to make corrections for drift, which was assumed to be linear; corrections were  $\leq 0.4 \text{ ‰}$ . Replicate analysis of showed that repeatability was  $\leq \pm 0.1 \text{ ‰}$  for solid reference materials and  $\leq \pm 0.2 \text{ ‰}$  for solutions made from them. The average repeatability of the analysis was  $\pm 0.06 \text{ ‰}$  for  $\delta^{13}\text{C}$  ( $n = 134$ ).

Microbiological analysis for thermotolerant coliform bacteria was conducted in the field. We analysed water, after purging, from 40 wells and 10 surface ponds in JAM, and 14 wells in the arsenic-free area of Mirathi, some 4 km to the north of JAM. The isolation and enumeration of the TTC was carried out using membrane filtration and growth on membranes with lauryl

sulphate broth (Oxoid, UK; Anon. 1994). The plates were incubated for  $\leq 4$  h at ambient temperature to aid bacterial resuscitation, before incubation at  $44 \pm 0.5^\circ\text{C}$  for between 16 and 18 hours. Yellow colonies were classified and counted as thermotolerant coliforms. Sanitary risks were quantified for each well in order to identify faecal sources, contaminant pathways and other factors that might contribute to contamination of wells (e.g. Lloyd and Bartram, 1991). Risk factors comprise observable faults in well construction and the proximity of sources of contamination, e.g. faecal material, and the distance between wells and latrines.

## 4. RESULTS

### 4.1 Sedimentology

A full description of the sediments and their composition will be presented elsewhere (Hudson-Edwards *et al.* in prep), so only an outline is given here (Table 1). Lithological logs of cored sediment were made on site and are reproduced in Fig. 2 without change. An upper aquitard of

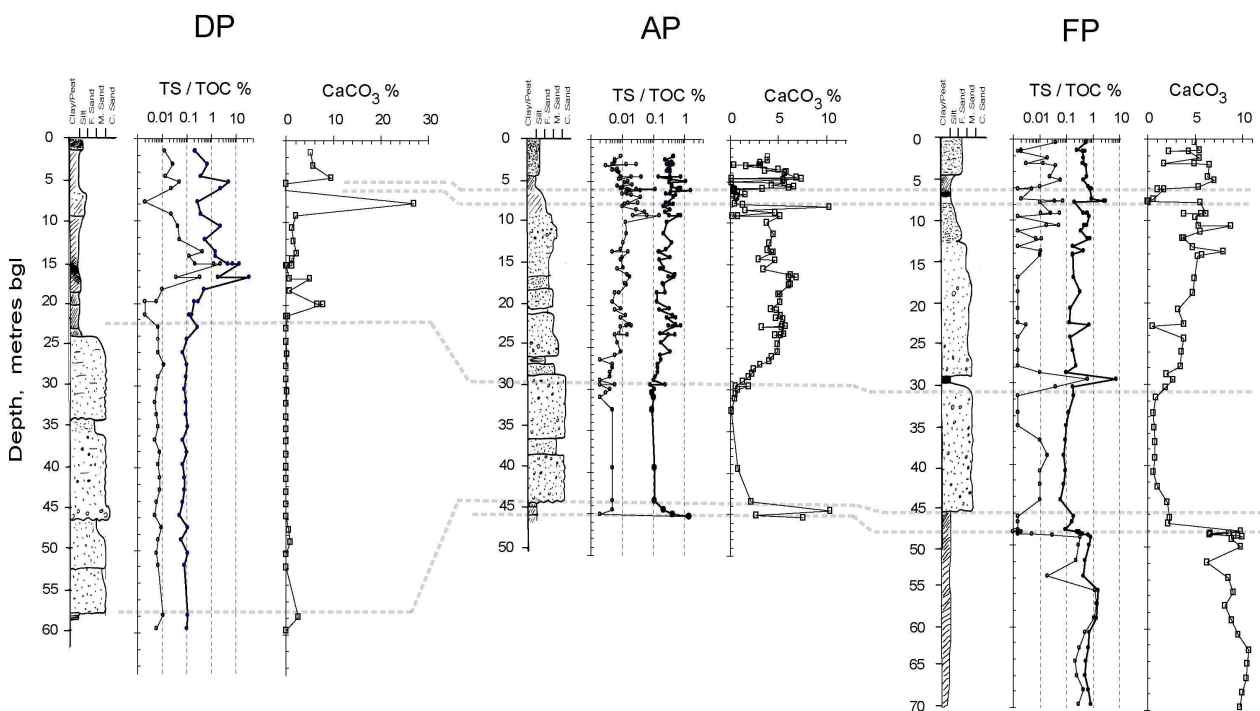


Fig. 2. Lithological logs and profiles of total organic carbon (TOC, bold line), total sulphur (TS, light line) and  $\text{CaCO}_3$  in sediment at piezometer sites DP, AP, FP, in JAM. Lithological logs are those made in the field and are reproduced without alteration. Lines of correlation are shown dotted. Note the logarithmic scale for TS and TOC.

silts and silty clays (Fig. 2), of variable thickness (9-24 m), overlies an unconsolidated sand aquifer between 32 and 36 m in thickness (the shallow aquifer): this aquifer is underlain by a clay aquitard about 25 m thick, beneath which is a deep aquifer that is  $> 60$  m thick.

The sediments were deposited between 22 000 and 1 200 years ago ( $^{14}\text{C}$  and OSL ages from Hudson-Edwards *et al.* in prep) by the Ganges/Brahmaputra Rivers and their distributary channels. Dating of quartz in cores from the AP site by the OSL method showed that the aquifer sands are  $> 17$  kyrs old below 32 m depth and  $< 8$  kyrs old above it (Hudson-Edwards *et al.*, 2004), which explains why it took 50 hammer blows to core 0.5 m of sediment at depths less than 32 m, but 90 below it; McArthur *et al.*, unpublished data).

Correlations between the piezometer sites are shown on Fig. 2 and are based on the abundance of calcite and organic matter (TOC) in the sediments. The aquifer at site DP, and the lower 13 m of

the aquifer at sites AP and FP, contains little or no calcite and almost no organic matter (<0.1%) and are therefore regarded as being of equivalent age (around 17000 years). In the upper aquitard, the calcite-free level around 6 to 8 metres depth in both AP and DP is assumed to correlate with the calcite-free level between 5 and 5.5 m in DP. Finally, in AP and FP, the upper few decimetres of the lower aquitard are brown and oxidised, and are assumed to correlate (drilling at DP did not reach to this level, so correlation to DP is not possible).

At site DP, in the east of the JAM area (Fig. 1), the upper confining layer is 24 m thick, with the lower half comprising impermeable clay (17 m to 24 m). A calcite-free interval occurs around 5 m depth. Above 17 m depth, the confining layer contains abundant organic matter, especially at depths of around 5, 15, and 17 m: the deepest occurrence comprises peat *sensu stricto* with a concentration of total organic carbon (TOC) of 34% (Table 1); the peat contained well-preserved tree-leaves. Sulphur concentrations in the OM-rich units reach 2.2% at 15.2 m depth, but is only 0.33% at 17 m depth. Calcrete occurs at 19.8 m. Around 21 m depth, the clay is brown and oxidised and shows on Fig. 2 as a minimum concentration of total sulfur: the oxidised unit passes gradationally downward into the underlying unoxidised grey clay. There is a sharp transition at 24 m into the underlying aquifer sands, which are brown in colour through the full thickness of the aquifer. The mean concentration of TOC in the aquifer sands is 0.09%, with no sample containing more than 0.11%, and the concentration of total sulphur in the aquifer sand does not exceed 0.012%. At the greatest depth reached (59.4 m), cuttings comprised brown sand mixed with grey silty clay, suggesting that the lower confining clay was nearby. However, the poor quality of sample from this depth made it impossible to discover whether the underlying aquitard had an oxidised upper surface as is the case at the other piezometer sites.

At AP, in southern JAM, the upper confining layer consists of silts and clayey silts. An interval free of calcite occurs between 6 and 8 m depth. Around 9 m depth, the silts grade downwards into fine sand in the upper part of the aquifer (Fig. 2). The aquifer sands are grey in colour above depths of 40 m, and brown in colour below it. Organic-rich units exist in the upper confining silts (1.6% TOC at 6 m depth; Table 1), and within the aquifer sands at 17 m (0.49% TOC) and 23 m (0.76 % TOC). In aquifer sands, the mean concentration of TOC is 0.27%. Concentrations of TOC appear to decrease with depth below a depth of about 23 m, but an uncored interval from 32.5 m to 38.5 m depth prevents certainty in this matter. Concentrations of total sulphur reach 0.12% in the upper confining silts but do not exceed 0.02 % in the aquifer sands. At a depth of 45 m, the aquifer sands give way abruptly to the underlying clay of the basal aquitard. The upper few decimetres of this aquitard are brown, oxidised, and contain < 0.1% TOC and < 0.001% of total sulphur. The oxidised horizon grades downwards into grey clay in which the concentrations of these constituents are higher. A similar oxidised upper aquitard occurs at FP (see below): at both sites, the total sulphur content of these intervals (Fig. 2) is low over several metres of the clay, suggesting that the oxidation is more pervasive than it appears.

At FP, in central JAM, the sediments consist of silts and clayey silts in the upper confining layer (0-12 m) that grade into mostly medium sand in the main part of the aquifer, which is 32 m thick. The upper aquitard is free of calcite between depths of 6 and 8 m. The aquifer sands are grey in colour, except at depths below 40 m, where hints of brown occur in a general grey colouration. Organic-rich units exist towards the lower part of the upper confining silts (2.9% TOC at 8 m depth; Table 1), and within the aquifer sands at 29.5 m (7.2% TOC). A single sample at 22.9 m depth contains 0.71% TOC and may represent a lateral equivalent of the organic-rich horizon at 23 m depth in AP. Elsewhere in the sands, concentrations of TOC seldom exceed 0.3% and are lower than this in the basal part of the aquifer. Concentrations of total sulphur reach 1.3% in the lower confining clay and 0.6% in the peaty unit at 29.5 m, but do not exceed 0.04 % in the aquifer sands, nor do they exceed 0.06% in the upper aquitard. The underlying aquitard of grey clay has been proven by drilling to be 25 m thick at this site. The upper part of this clay is brown

and oxidised, as it is at AP, and contains < 0.1% TOC and < 0.001% of total sulphur; it grades downwards into grey clay in which concentrations of these constituents are higher.

#### **4.2 Piezometer Waters**

The composition of water from the three piezometers (Figs. 3-5), which tap only the shallow aquifer, is presented in the order of increasing concentration of arsenic in the ground waters drawn from the aquifer (DP none; AP some; FP much), which is in the order of increasing concentration of organic matter in the aquifer sands (but not in the overlying aquitard; Fig. 2). The piezometer profiles reveal that the ground water is chemically stratified (Figs. 3-5), as expected (Parker *et al.* 1982; Karim *et al.* 1997; DPHE 1999; McArthur *et al.* 2001).

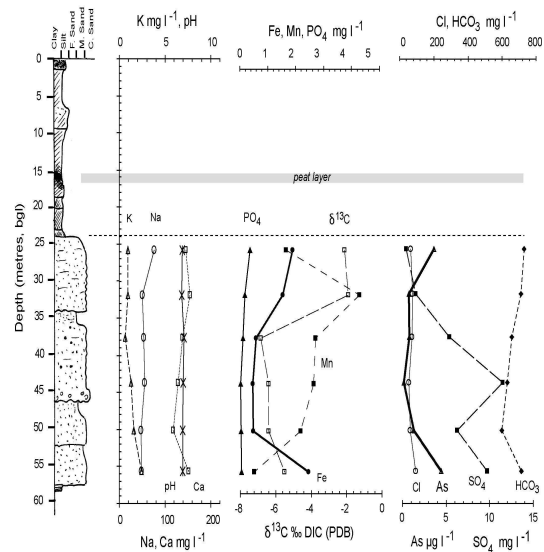


Fig. 3. Lithologic log and chemical profiles of groundwater composition in March, 2003, at site DP, Barasat, West Bengal. Horizontal dashed lines marks the boundary between the aquifer sands and the overlying confining unit; the base of the aquifer was not definitely reached, so no lower boundary is drawn. Note the very much thicker upper confining unit, and the very much lower concentrations of arsenic, compared to other sites (figs. 4,5). Alkalinity is reported as bicarbonate.

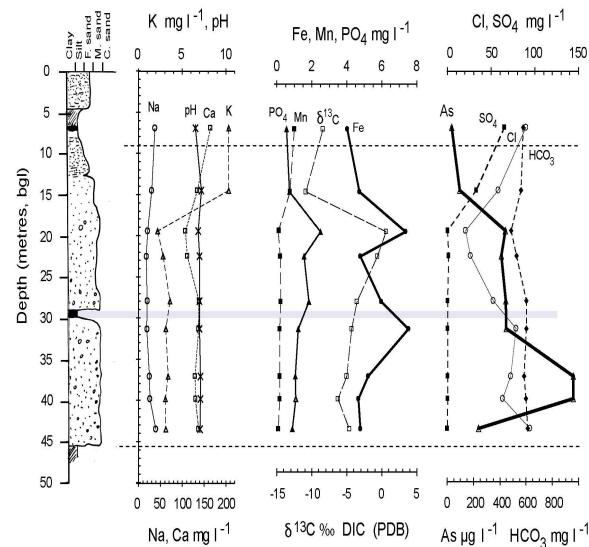


Fig. 4. Lithologic log and chemical profiles of groundwater composition in March, 2003, at Site AP, Barasat, West Bengal. Dashed lines mark the boundaries of the aquifer sands with confining units. The uppermost piezometer is screened within the silts of the upper confining unit. Alkalinity is reported as bicarbonate.

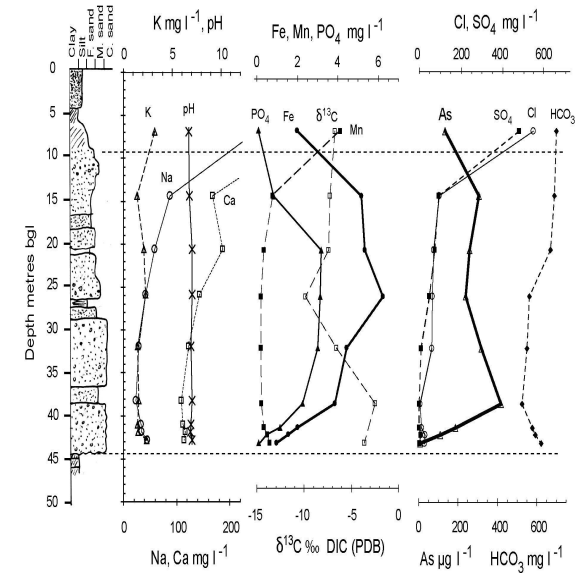


Fig. 5. Lithologic log and piezometer profiles of groundwater composition in March, 2003, at site FP, Barasat, West Bengal. Horizontal dashed lines mark the boundaries of the aquifer sands with confining units. The uppermost piezometer is screened in the silts of the upper confining unit. Alkalinity is reported as bicarbonate.



In the piezometer at DP, concentrations of aqueous arsenic do not exceed  $5 \mu\text{g l}^{-1}$  (Table 2; Fig. 3). Concentrations of Mn are high and peak in the middle of the aquifer at  $4.2 \text{ mg l}^{-1}$ , whilst concentrations of Fe show an inverse trend to those of Mn, being lowest in mid-aquifer ( $0.44 \text{ mg l}^{-1}$  at 43.7m) and highest ( $2.4 \text{ mg l}^{-1}$ ) in the lowest piezometer. Concentrations of phosphate are  $0.35 \text{ mg l}^{-1}$  at 25.8 m and decrease downwards. Concentrations of sulphate are higher than at our other sites and increase downward to be around  $10 \text{ mg l}^{-1}$  in the bottom half of the aquifer. Values of  $\delta^{13}\text{C}(\text{DIC})$  are around  $-2 \text{ ‰}$  in the upper part of the aquifer and  $-6 \text{ ‰}$  in the lower part and show no obvious relation to other parameters.

In ground water at AP from depths  $< 40 \text{ m}$  (Fig. 4), concentrations of iron ( $3.9$  to  $6.2 \text{ mg l}^{-1}$ ), phosphate ( $0.8$  to  $3.2 \text{ mg l}^{-1}$ ), and arsenic ( $240$  -  $420 \mu\text{g l}^{-1}$ ), are high. The maximum concentrations occur at depths of around  $38 \text{ m}$  (arsenic),  $26 \text{ m}$  (iron), and  $21 \text{ m}$  (phosphorus). The peak concentration for iron occurs just below the peak concentration of organic matter ( $0.72\%$  TOC) in the aquifer sands at  $23\text{m}$  depth. At  $26 \text{ m}$ , the value of  $\delta^{13}\text{C}(\text{DIC})$  also decreases by around  $2 \text{ ‰}$ , but overall values of between  $-2 \text{ ‰}$  and  $-10 \text{ ‰}$  are less negative than might be expected for a system so reducing. Towards the base of the aquifer (from the piezometer at  $38.3 \text{ m}$  depth downwards), concentrations of dissolved iron, arsenic, and phosphate decrease. Concentrations of sulphate decrease downwards from the uppermost piezometer, which is in the upper confining layers, and are  $< 10 \text{ mg l}^{-1}$  below  $32 \text{ m}$  depth.

In the piezometer waters at FP, concentrations of iron are high ( $4$  to  $7 \text{ mg l}^{-1}$ , Fig. 5) over the entire aquifer thickness, but are not related to those of dissolved arsenic nor to depth. Concentrations of arsenic are around  $430 \mu\text{g l}^{-1}$  in the upper part of the aquifer, but are much higher in most of the lower part ( $>32 \text{ m}$  depth), where they are  $>900 \mu\text{g l}^{-1}$  in a considerable thickness of the aquifer. Near the base of the aquifer (lowermost piezometer at  $43.4\text{m}$  depth), the arsenic concentration ( $239 \mu\text{g l}^{-1}$ ) is lower, but is still higher than it is in the base of the aquifer at AP ( $7 \mu\text{g l}^{-1}$ ). Values of  $\delta^{13}\text{C}(\text{DIC})$  range from  $+0.6 \text{ ‰}$  to  $-10.8 \text{ ‰}$  but shows no strong relation to lithology, including the presence of units rich in organic matter. Concentrations of sulphate decrease downwards from the uppermost piezometer (in the upper confining unit) and are  $< 1 \text{ mg l}^{-1}$  below  $25 \text{ m}$  depth. Concentrations of phosphate peak at  $2.5 \text{ mg l}^{-1}$  around  $20\text{m}$  depth and decline downwards.

### 4.3 Ground Water Flow

In the aquifers of the Bengal Basin, the natural flow regime combines three scales of flow-system, as described by Ravenscroft (2003). The first, at the kilometre scale in the shallow aquifer, is driven by local topography. On this is superimposed local systems, around microtopographic features such as levees, channels and ponds, that extend laterally for a few tens to perhaps a hundred metres, and vertically for  $10$  to  $20 \text{ m}$ . The third scale comprises natural flow to the south in the deeper aquifer.

Water levels in the piezometers at the three sites in the shallow aquifer, recorded in March 2003, are shown in Fig. 6: each has a perched water table in the upper aquitard. The head differences between the aquifer and overlying aquitard are  $0.32 \text{ m}$  at site AP,  $0.82 \text{ m}$  at site FP, and  $3.70 \text{ m}$  at site DP, and reflect the degree of hydraulic connectivity between aquitard and aquifer. Within the aquifer sands, piezometric levels vary by less than  $0.2 \text{ m}$ , and decrease downward, with the gradient being greatest ( $0.0013$ ) at site AP and lowest ( $0.0007$ ) at site DP. Ground water elevations in the lower part of the shallow aquifer indicate a hydraulic gradient of  $0.0006$  to the north north-east at the time of measurement - in the dry season in early March, 2003. During the monsoon season, the direction reverses as local rivers to the north and east fill with water (McArthur *et al.* unpublished piezometric data). Time-series measurements of hydraulic heads, and the hydrogeology of the area, will be presented elsewhere (Hudson-Edwards *et al.* in prep).

#### 4.4 Well Waters

In Table 3 we give the results of the chemical and microbiological analysis of the ground waters sampled from domestic and public wells. The compositions are typical of those found elsewhere in the Holocene sediments of the Bengal Basin (DPHE 1999; McArthur *et al.* 2001; Harvey *et al.* 2002; Dowling *et al.* 2003). Shallow wells in the central and northwest of JAM (Fig. 7) are rich in arsenic (200 - 1180  $\mu\text{g l}^{-1}$ ), iron (3 - 13.7  $\text{mg l}^{-1}$ ), and phosphate (1 - 6.5  $\text{mg l}^{-1}$ ), and lack manganese and sulphate, whilst a group of shallow wells (Ba14-18, Ba40-44) in the immediate vicinity of piezometer DP contain  $<10 \mu\text{g l}^{-1}$  of arsenic and more than 2  $\text{mg l}^{-1}$  of manganese. With few exceptions, high concentrations of arsenic are not spatially coincident with high concentrations of manganese (Fig. 7) nor with high concentrations of sulphate (Fig. 7), and these parameters are not correlated (Fig 8a, b).

In cross-plots (Fig. 8) of species affected by redox reactions (iron, sulphate) or iron reduction (arsenic, phosphate, iron), the data for shallow wells (excluding wells near the piezometer site DP, owing to their distinct sedimentological setting; Fig. 2) appear to fall into three groupings, on the basis of their As/Fe values, and their concentration of arsenic: those with  $< 17 \mu\text{g l}^{-1}$  of arsenic; those with  $> 32 \mu\text{g l}^{-1}$  of arsenic and high As/Fe; and those with  $> 32 \mu\text{g l}^{-1}$  of arsenic and low As/Fe. These three groups of wells appear to bear a relation to depth, a relation explained in a later section (Discussion). Wells with high As/Fe also have high As/ $\text{PO}_4$  (Fig. 8d) and distinctly less iron and phosphate (Fig. 8e) than do wells with low As/ $\text{PO}_4$  (Fig. 8 c,d,e).

The ground waters are anoxic because they contain dissolved iron. Concentrations of nitrate are generally  $< 1 \text{ mg l}^{-1}$  and the range in pH is small (6.76 to 7.32; Tables 2, 3). Strong correlations exist between dissolved concentrations of calcium, magnesium, and bicarbonate (Fig. 9a, b). Shallow wells have Na/Cl ratios that scatter widely about the value for marine-salt (Fig. 9c) showing that some wells have gained Na and some lost it, relative to chloride. Many wells plot along a trend of increasing calcium and sodium (Fig. 9d), as sodic feldspar and detrital calcite are weathered, but some plot to the right of this line, in a direction compatible with ion-exchange of Ca in solution for Na on mineral ion-exchange sites (trend of line B, Fig. 9d).

The deep ground waters are fresher (mean EC 753  $\mu\text{S cm}^{-1}$ ) than are shallow ground waters (mean EC 957  $\mu\text{S cm}^{-1}$ ): they contain less calcium, magnesium, chloride, and bicarbonate, but more sodium than most shallow wells (Fig. 9). Deep wells ( $>70\text{m}$ ) have higher Na/Cl and Na/Ca values than do shallow wells (Fig. 9c,d). Water from deep wells contains  $< 17 \mu\text{g l}^{-1}$  of arsenic.

Saturation indices, calculated for waters from shallow wells with Geochemist's Workbench (v. 3.0; Bethke 1998), show that most of the Joypur waters are oversaturated with calcite (SI +0.5 to +2.0), dolomite (SI +0.1 to +2.0) and aragonite (SI +0.1 to +0.5). Water samples with low concentrations of iron are at equilibrium or undersaturated with siderite (SI +0.2 to -0.9) and vivianite (SI +0.3 to -3), and at equilibrium or oversaturated with rhodochrosite (SI +0.02 to +0.7). By contrast, samples high in iron are saturated with vivianite (SI +0.8 to +3.7) and siderite (SI +0.3 to +1.5) and undersaturated with rhodochrosite (SI -0.3 to -1.3). Because Ba solubility is limited by the solubility of barite, concentrations of Ba in a few well waters (Tables 2, 3) approach the guideline value of 0.7  $\text{mg l}^{-1}$  (World Health Organization 1993) where concentrations of sulphate are low.

#### 4.5 Ground Water Abstraction

Inhabitants draw water for domestic supply mostly from private wells in the shallow aquifer, typically with 12-foot (3.6 m) screens that have their screen-centres at depths around 25 to 45 m, but 6 wells in our study area tap the deep aquifer ( $>70 \text{ m}$  depth). The deep aquifer is also

exploited by three irrigation wells near the JAM area: one is 600 m to its east, a second is 1000 m to the north, and the third is 200m to its southwest. The three deep wells irrigate 34 ha of agricultural land that borders the villages: the shallow aquifer is not used much for irrigation. During the development of both aquifers, abstractions must have modified the natural ground water flow regime. Nevertheless, natural flow at the kilometre scale appears still to dominate the shallow aquifer, as irrigation water is drawn from the deep aquifer only and shallow abstraction is but a small fraction of recharge. Deep abstraction for irrigation will induce regional down-flow through the clay aquitard between 45 m and 70 m, but its thickness ensures that the effect is small. Human modifications have applied, at most, for 40 years, whereas the natural flow regime has existed in its present form for up to 1 200 years, since this is the age of OM in the upper aquitards (Hudson-Edwards *et al.*, *in press*).

The deep irrigation wells to the north and east of the JAM area are screened from 100 to 130 m and pump for 8 hours a day in February and for 12 hrs a day in March and April to irrigate about 27 ha of rice and 7 ha of vegetables. The third, sited 200 m to the south west of the area, is 95 m deep and has a comparatively small abstraction. No abstraction volumes are available for these wells but, assuming typical crop water requirements (Ravenscroft 2003) and that deep percolation comprises 33% of abstraction, we estimate that the annual abstraction from these wells is of the order of 400,000 m<sup>3</sup>, with around 130,000 m<sup>3</sup> being returned to the shallow aquifer as deep percolation losses. Because of the clay aquitard at 45-70 m, the cone of depression created by these wells must have spread widely in the deep aquifer as downward leakage balances withdrawal of water from confined storage. In JAM, there are about around 100 hand tubewells taking water from the shallow aquifer. By assuming that each well is used by 10 people with an average water use of 20 l/d, the annual abstraction from the shallow aquifer is estimated to be of the order of 7,300 m<sup>3</sup>, which is 2% of the abstraction from the irrigation wells.

## 5. DISCUSSION

### 5.1 Piezometer Sediments

Our data and our correlations between the piezometer sites (Fig. 2) suggest that the sediments below a depth of 32 m in FP and AP are equivalent in age, and of the same age as the aquifer at DP; they also suggest that the sediment above 32 m in FP and AP is distinctly younger (< 8 ka) than underlying sediment, which is at least 17 kyrs old. The lack of calcite in sediment at DP, and below 32 m depth at AP and FP, might be due to its removal during oxidative weathering for a period of around 9 000 years prior to the deposition of overlying sediment, or to the deposition of the calcite-poor units by the Brahmaputra River: today, sediment of the Ganges River contains detrital calcite but sediment of the Brahmaputra River does not. This contrast is best seen by examining its reflection in the strontium content of ground water in Bangladesh (P. Ravenscroft; *Maps of Ground-Water Composition for Bangladesh*, <http://www/es.ucl.ac.uk/research/lag/as>): where detrital calcite occurs, concentrations of strontium in ground water are high (> 0.3 mg l<sup>-1</sup>); where calcite is absent, concentrations of strontium are low (< 0.3 mg l<sup>-1</sup>).

At DP, the aquifer sediments are brown over the entire depth of the aquifer. At AP, the aquifer sands are grey in colour (Fig. 10) above 40 m depth, and brown at greater depth. At FP, the sediments are grey throughout the full aquifer thickness (Fig. 10) but, at the very base of the aquifer (> 40m depth), the grey colour is accompanied by hints of brown at some levels (44.5 m). The upper few decimetres of the underlying aquiclude at AP and FP is also brown in colour and oxidised. As others have done (van Geen *et al.* 2003), we assume that the brown colour arises from the presence of FeOOH and that the grey colour occurs when these oxides have been destroyed (or given a sequestering surface coating) by reduction. Attempts to confirm this assumption, and to quantify the cause of the colour difference, using sequential chemical leaches were unsuccessful owing to uncertainty about the homogeneity, solubility, grain-size, and

crystallinity, of likely reduced phases and of FeOOH. Further work on this issue will be reported elsewhere (Hudson-Edwards *et al.* in prep.). Nevertheless, the colour difference does suggest an explanation for why concentrations of dissolved arsenic and iron seldom correlate well in ground water from alluvial aquifers where FeOOH-reduction is the dominant mechanism of arsenic release: it is that most of the Fe(II) that is reduced is sequestered in solid phases, such as; siderite (Pal *et al.* 2002), iron sulphide (Korte and Fernando 1991; Rittle 1995; Chakraborti *et al.* 2001) vivianite, magnetite (Harvey *et al.* 2002), and green rust (Frederickson *et al.* 1998). That not all reduced iron stays in solution is clear from the fact that the highest concentration of iron in our waters ( $13.7 \text{ mg l}^{-1}$ ; Table 3) requires the dissolution of only about  $2\text{-}3 \text{ mg kg}^{-1}$  of solid FeOOH. Although the amount of FeOOH in the sediment is low (see later), it is not that low: the reduction of FeOOH must, therefore, result largely in the production of solid phases containing Fe(II), with only a small fraction of the iron remaining in solution. The notable difficulty, then, in explaining the composition of ground water in alluvial basins is to account for instances (as found in JAM; see later) where dissolved iron and arsenic *do* correlate: the expectation is that they will not.

The brown colour occurs distally from the sources of organic matter, which are in the upper aquifer and overlying aquitard. At AP, only the base of the aquifer is brown (*i.e.* contains FeOOH), a level well below that where most of the organic matter is found. At site DP, the entire aquifer is brown, yet has abundant organic matter in the unit above it. An examination of that unit explains why: the upper confining layer is 24 m thick, but the lower half comprises impermeable clay (15m to 24m) which, despite its high content of organic matter between depths of 15.2 and 16.8 m (Table 1, Fig. 2), prevents hydraulic connectivity being attained between the peat and the underlying aquifer sands. The proof of the lack of downward transport is the presence of the brown clay at 21 m depth, which resulted from oxidative weathering; it has not been re-reduced during burial and the resumption of reducing conditions, as it would have been had organic-rich water from the overlying peat been percolating through it. The high water-level in the upper confining unit at DP ( $>3 \text{ m}$  higher than that at AP or FP ; Fig. 6) provides further proof of impermeability.

## 5.2 Piezometer Waters

The development of anoxia must be driven by consumption of oxygen and nitrate in the units rich in organic matter, and by the reductive effect of small organic molecules (carboxylic acids, amines, sugars), derived by fermentative degradation of the organic matter, which are dispersed through the aquifer (Bergman *et al.* 1999). Where the sediments contain FeOOH (DP, base of AP), concentrations of dissolved arsenic are low ( $<10 \text{ } \mu\text{g l}^{-1}$ ), despite the presence of dissolved iron which attests to a degree of reduction of FeOOH. We attribute these low arsenic concentrations to resorption, by residual FeOOH, of arsenic released by partial reduction of FeOOH. For example, towards the base of the aquifer at AP ( $>38.3 \text{ m}$ ), concentrations of dissolved iron, arsenic, and phosphate decrease markedly (Fig. 4). The iron concentration ( $0.97 \text{ mg l}^{-1}$ ) in the lowermost piezometer shows that reduction of FeOOH has occurred, but the brown colour of the sediment shows it has not gone to completion. The low concentration of arsenic in the lowermost piezometer at AP ( $7 \text{ } \mu\text{g l}^{-1}$ ) is therefore attributed to resorption of arsenic to residual FeOOH. Given sufficient time, organic matter migrating downwards will reduce all the iron oxide in the lower part of the aquifer at AP and release all of its sorbed arsenic to ground water, before continued recharge flushes the system clear of arsenic and other constituents.

A contrast between brown and grey coloration of sediment (particularly, between grey Holocene sediment and orange/brown Pleistocene sediment) and an association of brown coloration with low-arsenic water, has been noted in the area of Araihasar, Bangladesh (van Geen *et al.* 2003a), but in Araihasar, unlike in JAM, grey sediment does not always host arsenic-rich water. That a grey Holocene aquifer overlies a Pleistocene aquifer of a “deep burnt orange” colour was also noted in Munshiganj, Bangladesh (Harvey *et al.* 2002) but, again, low concentrations of arsenic

prevailed over much of the thickness of the grey Holocene aquifer. The differences between these sites and JAM awaits explanation.

The concentrations of arsenic in most of the lower part (37.0 – 39.8 m) of the aquifer at FP are higher ( $>900 \mu\text{g l}^{-1}$ ) than they are in the upper part of FP (94 –  $448 \mu\text{g l}^{-1}$ ) and are higher in both than they are at AP (maximum  $420 \mu\text{g l}^{-1}$ ). We attribute the differences to the fact that FP contains more organic matter than does AP, and higher peak concentrations of organic matter (e.g. 7.2 % at 29.5 m in FP, 0.76 % at 23m in AP). This additional organic matter must be driving reduction of FeOOH in FP further than it has gone in AP, and results in ground water with higher concentrations of both iron and arsenic. This organic distribution does not, however, appear to explain the fact that the maximum arsenic concentrations in AP and FP occur well below the maximum concentrations of phosphate and iron: the control on dissolved phosphorus and iron appears to be partially decoupled from the control on dissolved arsenic. The different depths of the maxima in arsenic, iron, and phosphate, is probably due simply to differences of the As/Fe/PO<sub>4</sub> ratios in the aquifer sands above and below 32 m, given their different hardness and age (see Results): variable lithology is a further reason why arsenic and iron seldom correlate well in ground water from alluvial basins.

In DP, the brown colour of the aquifers sands at all depths (Fig. 10) attest to the presence of FeOOH throughout the aquifer: that the composition of ground water is quite different from those at sites AP and FP is therefore not unexpected. Concentrations of arsenic are low ( $< 5 \mu\text{g l}^{-1}$ ), whilst concentrations of dissolved manganese and sulphate are high. The profiles and compositions at DP are best explained as resulting from the preservation of originally oxic connate water, which has subsequently been subject to creeping reduction as organic matter moves in laterally from surrounding sediments (e.g. site FP, which is 250 m to the west) to cause (presently) incomplete reduction of FeOOH and Mn(IV) oxides. Given the U-shaped profiles of arsenic, manganese and iron with depth (Fig. 3), organic matter must be diffusing upwards from the underlying organic-rich clay at this site (so its upper part cannot be oxidised?) as well as entering the aquifer laterally at shallow depths, so that the reduction potential decreases towards the mid-point of the aquifer: there, a peak in dissolved manganese (2-4  $\text{mg l}^{-1}$ , Fig. 3) coincides with a minimum in dissolved arsenic ( $< 2 \mu\text{g l}^{-1}$ ) and iron. Reduction of FeOOH dominates over reduction of manganese oxides towards the top and base of the aquifer. Concentrations of arsenic are kept low ( $< 5 \mu\text{g l}^{-1}$ ) by resorption of arsenic to residual-FeOOH. Oxides of manganese sorb arsenic (Manning *et al.* 2002; Foster *et al.* 2003), so the arsenic released by reduction of MnO<sub>2</sub> must be re-sorbed to residual oxides of manganese and iron, rather than remain in solution (as noted by Stüber *et al.* 2003).

The values of  $\delta^{13}\text{C}$  in dissolved inorganic carbon (DIC) are high for a redox-dominated system. They are kept from becoming more negative, and so from reflecting organic inputs more strongly, by the low pH of the ground water (6.76-7.32; Tables 2, 3), which promotes rapid equilibration between DIC and detrital calcite, with a  $\delta^{13}\text{C}$  around -1 ‰ (Table 1; Hudson-Edwards *et al.* in prep). At AP, values of  $\delta^{13}\text{C}(\text{DIC})$  decrease by around 2 ‰ at 26 m, a change that may reflect an organic contribution to DIC from the degradation of organic matter at 23m depth. At FP, the abundance of calcite approaches zero below 30 m depth; below this level, the more negative values of  $\delta^{13}\text{C}(\text{DIC})$  reflect this diminished buffering capacity (Table 1). Surprisingly, the organic matter at 29.5 m in FP appears not to influence values of  $\delta^{13}\text{C}(\text{DIC})$ . In the upper part of the aquifer at DP, values of  $\delta^{13}\text{C}(\text{DIC})$  around -2 ‰: they are around -6 ‰ at greater depth. These positive values must reflect equilibration with traces of calcite in the aquifer, although our analytical data suggests calcite is absent from DP.

At sites AP and FP, concentrations of sulphate decrease downwards from the uppermost piezometers, which are in the upper confining layers (Figs 4, 5), but we cannot say with certainty whether these profiles represent downward passage (dilution and dispersion) of recent

anthropogenic sulphate from the surface, infiltration of natural amounts of sulphate concentrated by evaporo-transpiration, or remobilisation of sulphur in iron sulphide from the organic-rich layers as oxic water passes through the uppermost part of the upper confining layers. It seems unlikely that they represent steady-state consumption of natural sulphate, at depth, by sulphate reduction, because the sites are < 350 m apart and would have similar near-surface concentrations were the profiles natural. In fact, concentrations at 7 metres depth are  $65 \text{ mg l}^{-1}$  at FP and  $490 \text{ mg l}^{-1}$  at AP. We speculate that the high concentrations of sulphate at 7 m at AP result from surface loadings of gypsum as a result of house building, as it is used in plaster and the locality has several substantial houses. If this is the case, the profiles imply that sulphate from a surface source can penetrate to 30 m depth within a few tens of years.

The chemical stratification revealed by our piezometers explains why wells may differ in composition despite being close to each other (< 5m) and of similar depth. Arsenic concentrations in the bottom four piezometers at the AP site decrease linearly with depth from  $419 \text{ } \mu\text{g l}^{-1}$  at 38.3 m to  $7 \text{ } \mu\text{g l}^{-1}$  at 42.8 m, a rate of change of  $92 \text{ } \mu\text{g l}^{-1} \text{ m}^{-1}$ . The rate is  $200 \text{ } \mu\text{g l}^{-1} \text{ m}^{-1}$  in the basal part of the aquifer at FP. Such high gradients will cause wells to differ substantially in arsenic concentrations if they differ by no more than a metre in depth, a distance within the uncertainty with which a driller would record the depth of a well.

Chemical stratification also compromises interpretations drawn from well-surveys of arsenic concentrations, in the Ganges Plain and elsewhere: low concentrations of arsenic in wells (*e.g.* as found near AP; Fig. 7) do not indicate that the aquifer they tap is free of arsenic: using local knowledge of aquifer colour, a driller may emplace wells in the small thickness of good water in the brown sand at the base of polluted aquifers, if it exists (as it does at AP). Consequently, arsenic in ground water would go undetected until breakthrough to wells, and its detection by analysis or the development of arsenicosis in consumers. Breakthrough and detection might be separated substantially in time and have serious consequences for health. Furthermore, the finding in an area of dangerous concentrations of arsenic in only a small percentage of randomly-distributed wells does not signal that the arsenic is localized and the aquifer generally safe for development: it may show only that most wells tap water from above or beneath a poisoned part of the aquifer.

### 5.3 Well Waters

The chemical stratification of the ground water in the shallow aquifer (Figs. 3-5), the differing depths of wells and the uncertainty about some well-depths, and the differing amounts of organic matter in the aquifer sands from place-to-place, conflate to obscure areal patterns in water quality (Fig. 7) and cross-plots of some dissolved constituents (Fig. 8): nevertheless, some patterns emerge. Wells near piezometer DP (14-18, 40-44) contain  $<10 \text{ } \mu\text{g l}^{-1}$  of arsenic and more than  $2 \text{ mg l}^{-1}$  of manganese, so the aquifer they tap must be sedimentologically and chemically similar to that seen in the DP piezometer, and be in a setting that is sedimentological distinct from those of other wells in the JAM area that lack manganese. The wells near DP must tap a part of the aquifer that is both free of organic matter and protected from direct infiltration of organic matter from above by a thick upper-aquiclude of clay. For wells near DP, the low concentrations of arsenic and iron, and the high concentration of manganese must be due to the fact that reduction of  $\text{MnO}_2$  dominates over reduction of  $\text{FeOOH}$ , and that where the latter occurs, it does not reduce all the  $\text{FeOOH}$ , so, in both cases, re-sorption keeps concentrations of arsenic low. That concentrations of arsenic are low when manganese is present is an observation not confined to the DP area: as Fig. 8a shows, arsenic and manganese appear to be largely mutually exclusive in solution, a situation that extends to most shallow wells within 2 km of the JAM area (McArthur and Banerjee, unpublished data) and more widely in Bangladesh (data in DPHE, 1999). High concentrations of manganese might therefore indicate the presence of arsenic-free connate water

in an aquifer where reduction of FeOOH is incomplete. The exploitation of water at such sites will constitute mining of a finite resource and may draw in arsenic-rich water. Such transport will be moderated by sorption to unreacted FeOOH. Regular monitoring of water quality is essential in such a complex situation.

The composition of wells away from site DP can be interpreted if it is assumed that the vertical pattern of chemical stratification in the aquifer across the rest of the JAM area resembles that seen at AP and FP. The assumptions are: that arsenic concentrations are low ( $< 50 \mu\text{g l}^{-1}$ ) where FeOOH is present to sorb arsenic; that this occurs only at the base of the aquifer; that arsenic concentrations reach a maximum at 35 – 40 metres and decrease sharply below this depth; that ground water above this depth contains less arsenic, although concentrations are still high; and that arsenic concentrations reflect the amount of reduction that has occurred, and so the amount of organic matter in the sediments. A well-by-well analysis of arsenic concentrations, however, does not reveal a clear relation between concentrations of arsenic and well depth, probably because some well-depths are wrong. There is, however, some relation between well-depth and both As/Fe and arsenic concentrations: if the lowest concentrations of arsenic ( $< 20 \mu\text{g l}^{-1}$ ) are assumed to represent wells emplaced in the base of the aquifer where FeOOH persists, as at AP, and if the remaining wells are divided into two groups on the basis of their As/Fe values, three divisions emerge (Fig. 8), *viz.*

Group A; nineteen wells with  $< 1 - 16 \mu\text{g l}^{-1}$  of arsenic.

Group B; twenty-four wells with  $> 32 \mu\text{g l}^{-1}$  of arsenic and As/Fe between 13 and 56.

Group C; twenty-four wells with  $> 32 \mu\text{g l}^{-1}$  of arsenic and As/Fe between 36 and 2025.

The mean well-depths for each group are:  $135 \pm 14$  feet (A);  $124 \pm 24$  feet (B); and  $108 \pm 20$  feet (C), where all uncertainties 1 s.d. Although these differences are not statistically significant, they are interesting because wells are constructed from 20-foot lengths of plastic pipe, topped by 3-6 feet of iron pipe. The mean depths of these three groups suggest that they reflect groups of wells that are mostly made with 7, 6, or 5 pipes, with 7-pipe wells (group A) being screened in brown sand at the base of the aquifer, 6-pipe wells (group C) being screened in the arsenic maximum seen in the piezometer profiles to occur in the lower part of the aquifer, and 5-pipe wells (group B) being screened above the arsenic maximum. The high standard deviation probably arises because some well depths are incorrect: nevertheless, enough are correct to allow the overall depth-control to be seen. The use of As/Fe, and arsenic concentrations, as a proxy for depth seems reasonable because the As/Fe values in AP and FP (Fig. 11) change with depth, reflecting the fact that the maximum dissolved concentrations of arsenic occurs at a depth greater than do those of iron or phosphate, which are themselves not much separated in terms of depth (Figs. 4,5).

The different As/Fe/PO<sub>4</sub> values present at different depths (Fig. 11) probably arises because the younger sediment ( $< 32$  m depth) releases more iron and phosphate on reduction, and less arsenic, than the older sediment ( $> 32$  m depth): such lithological differences, reflected in ground water composition, must be one reason why iron and arsenic often correlate poorly in the well waters of the Ganges Plain. Dividing the wells onto groups A-C, however, yields correlations in the arsenic-rich groups between arsenic and iron that are better than for the combined population, probably because the effect of mixing populations from different depths is reduced. The coefficient of correlation between arsenic and iron in the three populations (Fig. 8c) are: 0.01 for A ( $p = > 0.1$ ); 0.58 for B ( $p = 0.01$ ); and 0.86 for C ( $p = 0.001$ , if one outlier, with  $0.56 \text{ mg l}^{-1}$  and  $1131 \mu\text{g l}^{-1}$  of arsenic, is excluded); the pooled population has a coefficient of 0.58 ( $p = 0.001$  excluding the outlier). In a pooled population of 213 wells within 2 km of JAM, the correlation coefficient between iron and arsenic is 0.39 ( $p = 0.001$ ; Fig. 12; Banerjee and McArthur, unpublished data, 2003). If the correlations have meaning, it can be only because the lower and intermediate concentrations of arsenic, and the accompanying iron, reflect a dynamic process that

is proceeding extremely slowly, with the dissolved arsenic and iron concentrations representing a snapshot of slow, microbially-mediated release, prior to sequestration of iron into solid diagenetic phases and resorption of arsenic: the arsenic and iron are ‘kinetic species’ in the sense we use in Fig. 13 (see next section). Higher concentrations of arsenic may represent a state where all reactive FeOOH has been consumed, leaving the arsenic in solution with no sorber to adhere to: this idea is also developed in a later section. For groups A-C, the correlation coefficients between phosphate and iron (Fig. 8e) are 0.00 for A ( $p > 0.1$ ); 0.50 for B ( $p = 0.01$ ); and 0.62 for C ( $p = 0.001$ ): the coefficient for the pooled population is 0.72 ( $p = 0.001$ ) and is enhanced by mixing populations B and C, one high in phosphate and iron, the other lower in both. In a pooled population including data for 213 other wells within 2 km of JAM (Fig. 12; Banerjee and McArthur, unpublished data, 2003), the correlation coefficient between iron and phosphate is 0.76 ( $n = 213, p = 0.001$ ).

Given the discussion above, the high concentrations of arsenic and iron in the northwestern part of JAM (Fig. 7) is probably due to two factors *viz.* that most wells there are emplaced at a depth near to the arsenic maximum (are 6-pipe wells) and that organic matter around 30 m depth (as seen at FP) is more abundant in central and northwest JAM than it is elsewhere. In much of southern and eastern parts of JAM, concentrations of arsenic must be low ( $<50 \mu\text{g l}^{-1}$ ) because wells there are screened at the aquifer’s base in the small thickness of brown sand revealed at AP.

The considerations above show that real element associations can be disguised or enhanced by pooling data on too regional a scale, and that piezometer profiles are essential to a full understanding of the source, transport, and sinks, of arsenic in the Ganges Plain. This discussion also serves to emphasise that the results of well-surveys must be evaluated in combination with a knowledge of the local geology, particularly aquifer colour, and well depth.

#### 5.4 Diagenetic Iron Sulphide.

Diagenetic iron sulphide is a sink for dissolved arsenic (Korte and Fernando 1991; Rittle 1995), and is present in the sediments in West Bengal (Fig. 2; Chakraborti *et al.* 2001). As much of the ground water in the JAM area lacks sulphate, as do most ground waters in surrounding areas (McArthur and Banerjee, unpublished data, 2003) and in the Ganges Plain generally (DPHE 1999, 2001; Nickson *et al.* 2000, McArthur *et al.* 2001; Dowling *et al.* 2002), it must have been removed by sulphate reduction from most recharging water. As sulphate reduction is driven by microbial metabolism of organic matter, it is localised where organic matter is present. At all sites, total sulphur is almost absent from aquifer sands but is relatively abundant in the organic-rich units (Fig. 2; Table 1), which are (or have been) the site of sulphate reduction and formation of diagenetic iron sulphides. The traces of sulphur in the sands probably represents iron sulphide formed very early in the history of anoxia from reduction of sulphate in connate water. Reduction of sulphate is probably not occurring in the aquifer sands now, either because they lack sulphate (FP) or because sulphate-reducing bacteria are outcompeted by iron-reducing bacteria (Chapelle and Lovely 1992). The presence of sulphate in the upper aquifer at AP and FP (Figs. 4, 5), where it has penetrated to levels below some organic-rich units, might show that the organic matter has lost much of its original reducing power through biodegradation. From these arguments, and the fact that most of the organic-rich units are stratigraphically above arsenic-rich aquifers, we infer that little arsenic is being removed now from ground water in the aquifer sands by sequestration in diagenetic sulphide.

#### 5.5 Resorption as a Control on Aqueous Arsenic

*5.5.1 The Shallow Aquifer:* Knapp *et al.* (2002) showed that aquifer sands from Virginia, USA, sorbed sulphate least where FeOOH in the sediments had been removed from grain surfaces by



the establishment of reducing conditions. In JAM, arsenic concentrations are low where the sediments are coloured brown by FeOOH, and are high where sediments are grey because all FeOOH has been reductively consumed (Figs. 10). Reduction is incomplete in those parts of the aquifer that are distal from sources of organic matter (e.g. the base of the aquifer at AP), or where no hydraulic continuity exists between organic-rich sediments and aquifer sands (at DP). Where reduction is incomplete, resorption to residual FeOOH will keep arsenic concentrations low (as mooted by Ravenscroft *et al.* 2001), until all sorption sites become saturated by re-sorbed arsenic, or all FeOOH has been consumed: this idea is implicit in the model of Welch *et al.* (2000) that explains the generation of high concentrations of arsenic by progressive reduction of FeOOH. In Fig. 13, we show this model more explicitly: arsenic released to solution by reduction will exist in solution temporarily (we term this ‘kinetic arsenic’) until it is resorbed to residual FeOOH. Laboratory studies of microbial FeOOH-reduction show that arsenic resorbs over a timescale of a few days to weeks (Fig. 3B and 3C in Dowdle *et al.* 1996; Figs. 6 and 7 in Jones *et al.* 2000). Resorption will decouple concentrations of arsenic from those of iron and leads to poor correlations between these constituents: this is one reason why these constituents seldom correlate well in ground waters in alluvial aquifers. Resorption of arsenic will occur as ground water moves away from the influence of peaty sediment, where reduction is complete, to areas where it is not complete and FeOOH is available to sorb it (DPHE 1999).

*5.5.2 The Deep Aquifer:* resorption may be one reason why the deep aquifers in JAM, and widely across the Bangladesh, are free of arsenic (a very limited exceedance of  $50 \mu\text{g l}^{-1}$  of arsenic in deep wells may be explained as contamination or mis-identification of wells). Sands of the deep aquifer in Bangladesh are described as “burnt-orange” (Harvey *et al.* 2002) or as “yellowish-brown to pale grey sands...cemented by secondary clay and iron oxide” by P. Ravenscroft in DPHE (1999, Vol. S1 Main Report), because they were subjected to a long period of oxidative weathering during the lowering of sea-level that occurred between 125 ka and 18 ka (DPHE, 1999). This weathering must have generated FeOOH by oxidation of biotite and other iron-bearing minerals in the sediment. As a consequence, the higher content of FeOOH in Pleistocene sands of the deep aquifer distinguishes them (Stanley *et al.* 2000) from the Holocene sands of the shallow aquifer. We suggest that the establishment of anoxic conditions in the deep aquifer, as a consequence of the deposition of overlying, organic-rich, Holocene aquifers, has been sufficient to mobilise some iron into ground water (Table 3; DPHE 1999), but has been insufficient to reduce all its FeOOH, the remains of which may now act as a sorptive buffer to prevent arsenic from accumulating in solution. An alternative explanation for the lack of arsenic in waters from the deep aquifer, previously suggested by P. Ravenscroft in DPHE (1999), McArthur *et al.* (2001), and Ravenscroft *et al.* (2001), and repeated in Smedley and Kinniburgh (2002), is that sorbed arsenic was flushed from the deep aquifer during an extended period of oxidative weathering and flushing that occurred during the lowering of sea level between 125 and 18 ka. With available data, we cannot be certain which explanation is correct.

## 6. THE DRIVER FOR FeOOH REDUCTION

### 6.1 Natural Organic Matter in Sediments

*6.1.1. The JAM Area.* The data for the JAM area suggest that reduction of FeOOH is driven by natural, subsurface, organic matter, in organic-rich units, formed at the periphery of local peat basins, that are in hydraulic continuity with the aquifer. The concentrations of organic matter in JAM sediments (low % levels) is more than adequate to account for the amount of reduction present: at  $25^\circ\text{C}$  (the mean annual air temperature in JAM) infiltrating water contains around  $8.3 \text{ mg l}^{-1}$  of dissolved oxygen, an amount consumed by  $< 0.001\%$  of reactive organic matter in the sediment. That peaty sediment is connected with the presence of unwholesome water is

confirmed by local experience in JAM: Ashraf Ali (Ardivok driller, *pers. comm.*, 2003) has noted an association between bad water and ‘khalu mati’ (black soil, which we interpret to be peat, or peaty units) and between brown sediment and good water. The association suggests that connectivity (permeability) exists between aquifers and peat deposits in some parts of the Ganges Plain, perhaps where they are cut through by post-depositional channelling (H. Brammer, *pers comm.*, 2001).

In JAM, however, (where methane is not recorded) our DP profile shows that peat *sensu stricto* is encapsulated in impermeable clay: the deposition of the peat must have occurred in response to local waterlogging caused by the clay. The low permeability of this clay now prevents recharge from carrying soluble organic matter downwards into the underlying aquifer sands. The sediment profiles at FP and AP show that sites marginal to the peat depocentre (DP) developed lesser amounts of organic matter, in peaty layers that are lateral extensions of the main peat (*i.e.* are of a similar age; Hudson-Edwards *in press*). In these marginal environments, the thinner, perhaps intermittent, clay will allow a degree of hydraulic connectivity with underlying aquifer sands and so allow ingress of organic matter. During sedimentation, however, such sites would have been less waterlogged and so would have accumulated less organic matter than basin centres, and so would host less organic matter. Beyond the basin margin, permeability will be higher, but the amount of organic matter will be negligible. We illustrate our idea in Fig. 14, where a schematic cross-section through the JAM area shows the relation of permeability, organic matter, and sedimentary architecture. This model suggests that chemical reduction in the JAM aquifer (and, by implication, elsewhere in the Bengal Basin) is driven by organic matter in peaty units that develop on the margins of peat basins where there is enough organic matter to drive redox, and sufficient permeability to allow organic matter to invade the aquifer in soluble form.

*6.1.2 Other Areas in the Bengal Basin.* The coincidence of high concentrations of arsenic in groundwater and wetland environments, where plant productivity is high, was noted by Ravenscroft (DPHE 1999) and has been reproduced in Smedley and Kinniburgh (2002), whilst both McArthur *et al.* (2001) and Ravenscroft *et al.* (2001) argued that peat, which forms in such wetlands, was the driver for reduction of FeOOH in the Bengal Basin. One reason for an emphasis on peat is that methane in combustible amounts is found at depth in some ground waters (Ahmed *et al.* 1998; Harvey *et al.* 2002) and the fact that methane in such amounts can be generated only by anoxic degradation of high concentrations of organic matter. If organic matter, accumulating marginally to peat depocentres, drives reduction of FeOOH (and so arsenic release to ground water) it is crucial to establish the extent of peat deposition in the Bengal Basin..

Peat is common beneath the Old Meghna Estuarine Floodplain in Comilla (Ahmed *et al.* 1998), Sylhet, and the Gopalganj-Khulna Peat Basins (Reimann 1993; Brammer 1996). Many wells in the area around Faridpur may be screened in waterlogged peat (Safiullah 1998) and the shallow aquifer system in Lakshmipur contains peat (DPHE 1999). Peat is often found in geotechnical borings (piston samples), although it is rarely recorded during rotary drilling for water wells because such drilling masks its presence, unless the peat is very thick. Peat occurs extensively beneath the arsenic-affected areas of southern Samta village and Deulhi village in southwestern Bangladesh at a depth of about 10 m (AAN 2000, Ishiga *et al.* 2000). Peat has been found in Holocene sediments around Mymensingh (Ishiga *et al.* 2000) and is well documented at Panigati, in SW Bangladesh (Islam and Tooley 1999). Organic-rich sediment has been reported to occur at 6 m and 25 m depth in Faridpur and at 28m depth in Sonargaon (Fig. 3 of Tareq *et al.* 2003). Sediment from a depth of 2.1 m at Gopalganj (100 km SW of Dhaka) contained 6% TOC (Nickson *et al.* 1998); sediment from a depth of 23m at Tepakhola (Faridpur municipality) contained 7.8% TOC (Safiullah 1998). Peat is repeatedly mentioned by Umitsu (1987, 1993) and by Goodbred and Kuehl (2000) as being present in Bangladesh sediments; it has been reported to occur in southern West Bengal by Banerjee and Sen (1987), and also by Pal *et al.* (2002) who note that peat was present in the subsurface in an arsenic-free area, but not in a nearby arsenic-

affected area. These authors do not state whether their peat was underlain by impermeable strata, as at our DP site, but it seems likely. It could be that the apparent lack of peat at their arsenic-affected site means that it was missed during coring. Harvey *et al.* (2002) also reported that no peat was found at an arsenic-affected site in Bangladesh, but they report the presence of methane (marsh gas) in combustible amounts; this proves the presence of much organic matter in the aquifer close to their site.

Thus, in the Bengal Basin, peat deposits are widespread, and so the margins of such deposits must be common. Despite the importance of peaty sediment as the redox driver in the Ganges Plain, there are two other potential drivers of redox: these are organic waste in latrines (McArthur *et al.* 2001; Ravenscroft *et al.* 2001), and organic matter leached from surface sources, such as soils, river beds, and ponds (Harvey *et al.* 2002). We consider each in turn.

## 6.2 Other Sources of Organic Matter

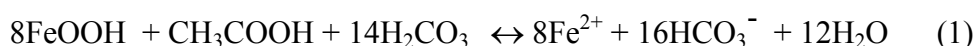
**6.2.1 Organic Matter in Latrines.** Human organic waste in latrines does locally promote reduction of FeOOH in aquifers and so contributes arsenic to groundwater, thereby confusing the regional signal of pollution derived from reduction by natural organic matter. The impact of point-sources can be seen in Singair, an arsenic hot-spot in Holocene sediments some 10 km west of Dhaka, Bangladesh: of 15 shallow wells within 300 m of Singair mosque (Safiullah and McArthur, unpublished data, 2001), the 3 wells sited within 3 m of latrines contained  $900 \mu\text{g l}^{-1}$  of arsenic, whilst the remaining 12 wells, all  $> 15$  m from latrines, contained between 100 and  $300 \mu\text{g l}^{-1}$  of arsenic. Such an influence is not uncommon; new wells drilled *through* new concrete pit-latrines have been observed (McArthur 2001, unpublished data). Point sources will be particularly strong where the polluting organic matter is in hydraulic continuity with the aquifer *e.g.* where the depth of a latrine is greater than the thickness of the upper confining layer and/or where wells and latrines are adjacent. But organic matter in latrines cannot be the main driver of arsenic pollution of ground water because it is free of arsenic in many areas of Bangladesh, despite the fact that the country is densely, and fairly evenly, populated.

The impact of human sources of organic matter will be small, or negligible, where: the depth of pit latrines is less than the thickness of the upper confining layer; wells are far from latrines; sewage collection is engineered; the unsaturated zone is very thick (as it is on parts of the Madhupur and Barind Tracts). Such is the case in JAM, where many dwellings have concrete-lined holding tanks with tops above ground level and where the depth of the upper confining layer is between 9 metres (at FP and DP) and 24 m (at DP). Several considerations suggest that there is little connectivity between latrines and aquifer water in JAM. Firstly, thermotolerant (faecal) coliforms (presumptive *E. coli*), are bacterial indicators of faecal pollution. Despite the very high risks of faecal pollution from poor well-completion, open access of many wells to animals, and the fact that there is generally a broad relationship between log(TTC) and sanitary risk scores (Cronin *et al.*, 2003), our wells mostly have a low TTC count (Table 3; summary statistics in Table 4): about 85% of our wells contained  $< 10$  cfu/100ml of water. Furthermore, there is no correlation between TTC count and arsenic concentrations in JAM wells. Given the high number of observable risks to JAM wells, their low TTC counts probably stem from the fact that most are  $> 30$  m deep, are sealed around the annulus by the clayey silt of the thick ( $\geq 9$  m thick) upper confining layer, and many have concrete completions of good quality, although the completions are mostly small in diameter. These factors reduce access of microbially-polluted water into the aquifer *via* the annulus of the well. The implications of these results is that microbial contamination of the aquifer in the JAM area is on a small scale and so organic pollution of the aquifer by human waste is limited in volume and distribution. Hence, it is unlikely that faecal organics do much to drive reduction of FeOOH in JAM aquifers.

**6.2.2. Surface Sources of Organic Matter.** For reasons given above, it seems unlikely that reduction of FeOOH in the JAM area is driven by surface sources of organic matter (rivers, ponds, and soils), drawn into the aquifer by irrigation drawdown, as has been suggested to occur in Bangladesh by Harvey *et al.* (2002). We note, however, that the occurrence of methane in combustible amounts around 30 m depth in Munshiganj, but in lessening amounts as depth diminishes (Harvey *et al.* 2002), and the presence of methane in ground water elsewhere in the Ganges Plain (Ahmed *et al.* 1998), can be due only to the presence of subsurface organic matter in high concentrations. Furthermore, if surface sources of organic matter in the Ganges Plain were of much importance in driving the release to ground water of large amounts of arsenic, high arsenic concentrations would not be confined to about 25% of wells (DPHE 1999), or to Holocene sediments (it is largely absent from the Barind and Madhupur Tracts; DPHE 1999; McArthur *et al.* 2000; Ravenscroft *et al.* 2001), nor would they be highest around 20 to 40 m depth across most of the Ganges Plain (*ibid*, Harvey *et al.* 2002; Karim *et al.* 1997; van Geen *et al.* 2003a). Finally, although the  $^{14}\text{C}$  ages of Harvey *et al.* (2002) for DIC show that very young water is penetrating to depths of around 20 m, the piezometer profiles of those authors show that concentrations of dissolved organic carbon (DOC) increases with depth to around 30 m depth, below which they scatter but remain high to 80 m depth, thereby proving the DOC has a deep source. The arsenic maximum (and a maximum concentration of methane) at 35-40 m depth cannot be caused by organic matter migrating downwards *against* a concentration gradient and then reacting at depth. The discrepancy noted by Harvey *et al.* (2002) between young  $^{14}\text{C}$  ages for DIC, and older  $^{14}\text{C}$  ages for DOC, is explicable in terms of a reservoir age for DOC and its derivation from older buried peat.

### 6.3 The Capacity to Reduce FeOOH

The results and discussion given here provide strong evidence that reduction of FeOOH across the Ganges Plain is driven overwhelmingly by buried, natural, organic matter. According to the equation for reduction of FeOOH, where FeOOH is used to represent iron oxides:



Given: the stoichiometry of this reaction; a density of 1 for buried peaty sediment; a carbon content of 7% in the sediment; a thickness of 50 cm for a peaty layer (as at 29.5 m depth in FP) with half the carbon bioavailable; and a porosity of 40%, then there will be about 1.1 g of bioreactive carbon under each  $\text{cm}^2$  of aquifer. The organic matter will consume 25 g of FeOOH which, given a porosity of 40%, a density of FeOOH of 2.4, and an aquifer containing 0.2% FeOOH, will be contained in an 8 m thickness of aquifer sand, which is half that of the aquifer thickness at FP below the peaty layer at 29.5m depth, and is similar to the thickness in which concentrations of arsenic exceed  $900 \mu\text{g l}^{-1}$ . Towards the base of the aquifer at FP, concentrations of arsenic decrease whilst remaining high. Our calculation is very basic, but suggests that few aquifer volumes of water have passed vertically through the sands: had they done so, the organic matter, or the FeOOH, would be exhausted by now and the aquifer would be clear of both dissolved iron and dissolved arsenic.

Although approximate, the calculations above suggest (and observation confirms) that there is enough organic matter in our aquifers in JAM for the entire aquifer thickness to be at risk: confusing the calculation are three factors. Firstly, the organic matter in the sediments at JAM is  $\geq 1$  200 years old (Hudson-Edwards *et al.* 2004), so it has been degrading for a substantial period of time. On deposition of the sediment, the amount of organic matter would have been greater and it would have been fresher, and more biodegradable, than it is now. Secondly, there is some uncertainty regarding the estimate of 0.2% for the amount of FeOOH in the aquifer. This figure represents the iron, recalculated to FeOOH, that is leachable by ammonium oxalate at pH 3 (Table 5) from sands in mid-aquifer at site DP, which is the least reduced of the three piezometer sites (Figs. 3-5, 10). The figure of 0.2% is a maximum because the leaches contained phosphorus,

sulphur, aluminium, iron, magnesium, (but not calcium, because calcium oxalate is insoluble) and it is not possible to apportion the leachable iron between FeOOH and possible diagenetic phases formed by its partial reduction *viz.* magnetite, green rust, vivianite, siderite, iron sulphide (Lovley *et al.* 1987; Frederickson *et al.* 1998; Chakraborti *et al.* 2001; Glasauer *et al.* 2003), or to possible detrital phases such as Fe-rich chlorite. Thirdly, the formation of magnetite ( $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ ) by reduction of sedimentary FeOOH reduces only one-third of the available pool of Fe(III) whilst sequestering the remaining two-thirds in the mineral structure (Frederickson *et al.* 1998, para 4, page 3249) where it may be unavailable for reduction. Thus, the availability of FeOOH to sorb arsenic in Bangladesh sediments will be some 70% less than supposed if magnetite is the main product of FeOOH reduction across the Ganges Plain. It can be inferred from the results of Harvey *et al.* (2002) that magnetite comprised most of the iron that was extractable with oxalic acid solution from aquifer sediments from , Bangladesh, and so magnetite constituted up to 6% of total-Fe (although this inference is compromised by uncertainty about whether the mineral formed by oxidation of green rust during storage, or by reduction in the aquifer).

## 7. OTHER MECHANISMS OF ARSENIC RELEASE TO GROUND WATER

This study confirms that reduction of FeOOH is mechanism that explains arsenic pollution of anoxic ground water in the Ganges Plain and, by implication, worldwide, since reduction of FeOOH is not a site-specific process. Other mechanisms, such as reductive dissolution of manganese oxides (Smedley and Kinniburgh 2002), competitive exchange with bicarbonate (Appello *et al.* 2002), and pH-dependent desorption from, or recrystallization of, FeOOH (Welch *et al.* 1988, 2000; Smedley and Kinniburgh 2002), are not needed, for the reasons given below.

### 7.1 Reduction of Manganese Oxides

The reduction of manganese oxides is thermodynamically more favourable than is the reduction of FeOOH (Edmunds 1986; Stüben *et al.* 2003) and occurs before it. It follows that arsenic, originally sorbed to manganese oxides but released by reduction, must be resorbed to FeOOH (or residual manganese oxides) rather than be released to ground water (Stüben *et al.* 2003). We concur with this view, noting that in JAM wells, concentrations of dissolved arsenic are low ( $< 33 \mu\text{g l}^{-1}$ ) where concentrations of manganese exceed  $1 \text{ mg l}^{-1}$  (Table 3; Fig. 8a). Our conclusion, and that of Stüben *et al.* (2003), are contrary to that of Smedley and Kinniburgh (2002), who state that “Manganese oxides also undergo reductive desorption and dissolution and so could contribute to the As load of ground waters in the same way as Fe”, because these authors did not recognize one of the most important controls on arsenic concentrations in ground water – resorption to FeOOH.

### 7.2 Exchange of Sorbed Arsenic with Bicarbonate in Ground Water

Severe pollution of ground water by arsenic is not common, and is particularly uncommon in potable water from oxic aquifers, in which bicarbonate is the commonest and most abundant anion worldwide: it follows that the suggestion that arsenic is released to solution by competitive exchange with bicarbonate (Appello *et al.* 2002) is unlikely to be correct. Ground waters from a variety of aquifer types in the UK contain bicarbonate in concentrations of hundreds of milligrammes per litre, yet arsenic concentrations are typically  $< 10 \mu\text{g l}^{-1}$  and natural concentrations above  $50 \mu\text{g l}^{-1}$  are rare (BGS 1989). Moreover, concentrations of bicarbonate in JAM are highest ( $744 \text{ mg l}^{-1}$  at site DP, Table 2; Fig. 3) where the ground water contains less than  $5 \mu\text{g l}^{-1}$  of arsenic. Furthermore, the large range of arsenic concentrations at AP and FP bear no relation to concentrations of bicarbonate (Figs. 4, 5): this is best seen in the lower part of the aquifer at AP (Fig. 15), where concentrations of arsenic decrease from  $419 \mu\text{g l}^{-1}$  (38.3 m) to 7

$\mu\text{g l}^{-1}$  (42.8 m) whilst pH varies by less than 0.2 units, bicarbonate increases from 526 to 622  $\text{mg l}^{-1}$ , dissolved silica (as  $\text{H}_4\text{SiO}_4$ ) varies by only 4  $\text{mg l}^{-1}$ , dissolved phosphate decreases from 2.3 to 0.13  $\text{mg l}^{-1}$ , and dissolved iron decreases from 3.9  $\text{mg l}^{-1}$  to 0.97  $\text{mg l}^{-1}$ . These data emphasise the minimal role played by pH, bicarbonate, and silica, in affecting concentrations of arsenic in ground water in JAM and, by implication, in sediments elsewhere. Competitive exchange with natural organic matter (Redman *et al.* 2002), or other ligands (*e.g.* silica), may become important when considering mechanisms of arsenic release that lead to concentrations of arsenic of  $< 50 \mu\text{g l}^{-1}$  but, even at low concentrations, partial reduction of FeOOH and release of kinetic arsenic (arsenic released by reduction but soon resorbed to residual FeOOH, Fig. 13) may be adequate to explain low concentrations of arsenic in anoxic environments.

### 7.3 Desorption of Arsenic Induced by Increasing pH

Sorption of arsenic to solids, notably sedimentary FeOOH, is generally held to be pH dependent, leading to the suggestion that desorption of arsenic from mineral surfaces may contribute arsenic to ground water as pH rises (Welch *et al.* 1988, 2000; Robertson 1989; Smedley and Kinniburgh 2002). A general observation that waters of higher pH tend to have higher concentrations of arsenic (Welch *et al.* 1988; Robertson 1989) is not in itself adequate to prove a causal connection between the two: other factors, such as residence time, evaporation, and weathering, may cause an increase in both. Whilst pH-dependent desorption may release arsenic to ground water in plumes of landfill leachate, or hydrocarbons, where pH can exceed 10, there is little direct evidence that this process releases arsenic to potable ground water, in which pH rarely exceeds 8.5. In waters from JAM, arsenic concentrations range from  $< 1$  to 1180  $\mu\text{g l}^{-1}$ , despite the narrow range of pH (6.8 to 7.3; Table 3), a fact best illustrated by data from the base of the AP site (Fig. 15). It follows that pH is not a control on any sorption or desorption of arsenic that may occur in JAM aquifers.

Arsenic concentrations were linked to pH by Welch *et al.* (1988): the mechanism of pH-dependent desorption was used by Robertson (1989) to explain the presence of arsenic in oxic potable ground water from 24 alluvial basins in Arizona, and has since been widely invoked. Robertson (1989) noted that concentrations of arsenic increased as pH increased along flowlines in aquifers in several alluvial basins, and assumed the relation was causal. Many indicators in his data suggest otherwise: in the Verde Valley ground waters, arsenic concentration decreased with increasing pH (as he noted); the overall correlation-coefficient between pH and arsenic concentration for his 24 sites was low (0.18,  $n = 456$ ; his Table 2); salinity increased along flowlines by a factor of between 4 and 8 (judged from his Fig. 3) suggesting either extensive evaporo-concentration, mixing with deeper more saline waters, or weathering, occurred as the water passed down the aquifer. It seems likely that arsenic accumulated in solution along some flowlines in response to in-situ weathering of volcanic rocks, and that the accompanying increase in pH was a consequence of such weathering, not a cause of arsenic accumulation. Robertson (1989, p. 183) noted that “the basins containing the largest concentrations (of arsenic) are bounded primarily by basalt and andesite” and so the basin-fill must be weathered materials from those rocks, which may have moderated the concentrations by resorption to weathered sediments. Robertson’s observation that concentrations of arsenic correlated well with concentrations of molybdenum, fluoride and vanadium, at sites examined in detail, parallels the observation of Nicolli *et al.* (1989) that arsenic, fluorine, and vanadium, are associated in arsenic-polluted ground water in central Argentina; both the association and the arsenic pollution were ascribed by Nicolli *et al.* (1989) to the weathering of dacitic volcanic ashfall layers in the loess aquifers.

The relation of pH to arsenic in solution can be further illustrated by reference to ground waters in aquifers of metamorphic bedrock in New England, USA (Ayotte *et al.* 2003). Higher concentrations of arsenic ( $>10 \mu\text{g l}^{-1}$ ) occur in waters with higher pH (7.5 to 9.3), but many samples, with pH ranging from 5 to 8.8, contain  $< 2 \mu\text{g l}^{-1}$  of arsenic (Fig. 4 of Ayotte *et al.*

2003): this would not be the case if arsenic concentrations were linked to pH-related desorption. These authors note that the primary control on arsenic concentrations is bedrock type. Furthermore, concentrations of arsenic in UK aquifers are not related to pH (BGS 1989): concentrations of  $< 4 \mu\text{g l}^{-1}$  occur in aquifers with a pH range from 7.0 to 9.5 (*e.g.* the Lincolnshire Limestone, Table 5.3 on page 83 of BGS 1989) and concentrations rarely exceeded  $50 \mu\text{g l}^{-1}$ , whatever the pH. Thus, the observation made by Welch *et al.* (1988) of a weak positive correlation between pH and concentrations of arsenic in a large dataset of compositions of US ground waters may have explanations other than pH-induced desorption.

Finally, Dixit and Hering (2003) show that sorption of both As(III) and As(V) to iron oxides becomes less sensitive to pH as arsenic concentrations, and  $\text{As}_{\text{aq}} / \text{Fe}_{\text{sediment}}$  ratios, decrease. At their lowest arsenic concentration ( $750 \mu\text{g l}^{-1}$ ), which approaches those found in the Ganges Plain, these authors showed that sorption is almost independent of pH over the range of pH common in most ground waters. Their data confirm that pH-dependent sorption does not contribute significantly to the release of arsenic to anoxic potable ground waters of the composition, pH-range, and salinity typical of potable waters from alluvial aquifers.

## 8. THE HIMALAYAN CONNECTION

### 8.1 The Bengal Basin

We postulate that the widespread occurrence of arsenic concentrations above  $100 \mu\text{g l}^{-1}$  occurs only when sorption sites for arsenic in an aquifer are saturated *i.e.* when reduction of FeOOH has gone largely to completion. Because high concentrations of arsenic are common in Holocene sediments of the Bengal Basin, they evidently have a particular susceptibility to undergo complete reduction of FeOOH: we explain this as follows. The Holocene sediment in the Bengal Basin derives from Himalayan rocks that are (mostly) igneous and metamorphic. Other than adjacent to the Indo-Burman ranges, surface coatings of FeOOH, with sorbed arsenic, are not inherited from previous erosional cycles but must be created from crystalline rocks by weathering. The aquifer sands derive largely from erosion at a time of extended glaciation in the Himalayas when physical weathering dominated and the intensity of chemical weathering was limited by the low (glacial) temperatures during erosion. The immature sediment was transported rapidly to the lower reaches of the basin and buried in a waterlogged, anoxic environment and so had little opportunity to acquire much FeOOH through oxidative weathering. Further, much of the fine fraction was winnowed during transport and deposited offshore, thereby reducing the surface area of sediment available to host coatings of FeOOH. The abundance of fresh-looking muscovite and biotite in the Holocene sediments attests to the limited degree of chemical weathering they have undergone. Older sediments, such as the deep aquifer in Bangladesh, and sediment at DP, and below 32 m depth in JAM, has suffered more weathering.

In Table 5, the content of diagenetically-available iron (as acid-oxalate leachable iron) in oxidised brown sediments from JAM (from the base of the aquifer at AP, and from DP) is compared to that in sediments from elsewhere and shown to be low ( $< 0.2\%$ ) in comparison. As the only brown sediment at depth in JAM is of pre-Holocene age, and has probably suffered a period of oxidative weathering that would have increased its content of FeOOH, the original Holocene sediment may have contained even less. Admittedly, such comparisons are fraught with uncertainty: the leachable iron may be in vivianite, green rust, magnetite, iron sulphides, chlorite, and carbonate, as well as in oxides. Nevertheless, this data lends some support to the idea that the Ganges Plain is severely polluted by arsenic because its sediments contain little FeOOH (to sorb arsenic) but have a superabundance of organic matter with which to reduce it, so that total reduction is common. In this context, the comment of Harvey *et al.* (2002, p. 1604), that grey-coloured sediment in an arsenic-polluted profile in the Ganges Plain “contains little, if any, purely

ferric [Fe(III)] oxyhydroxides”, confirms that, where high concentrations of arsenic are common, reduction of FeOOH has gone effectively to completion.

## 8.2 Implications for Other Areas

In aquifers that contain much FeOOH and/or little organic matter, reduction of FeOOH will be incomplete and the release of arsenic by reduction will be moderated by resorption to residual FeOOH. Such a process may be moderating arsenic concentrations in groundwater in, for example, the alluvial aquifers of the Tualatin Basin, Oregon (Hinckle 1997), where ground waters contain modest concentrations of arsenic ( $<1$  to  $73 \mu\text{g l}^{-1}$ ), and where those that exceed  $50 \mu\text{g l}^{-1}$  also contain some iron ( $0.16$  to  $1.9 \text{ mg l}^{-1}$ ) and phosphate ( $0.36$  to  $2.0 \text{ mg l}^{-1}$ ). Hinckle and Polette (1999) speculated that FeOOH reduction was one plausible mechanism of arsenic release to ground water in reduced ground waters of the basin. We agree, but add that resorption of arsenic to residual FeOOH has probably kept its concentration low. A more extreme example of resorption control may occur in alluvial aquifers of eastern Arkansas, where ground water contains up to  $42 \text{ mg l}^{-1}$  of dissolved iron, but less than  $52 \mu\text{g l}^{-1}$  of arsenic (Kresse and Fazio 2003). Although the aquifer sediments contain lignite and peat, the amount of organic matter available (*i.e.* biodegradable) appears to have been insufficient to reduce all the sedimentary FeOOH, so concentrations of arsenic are probably being moderated by resorption to unreduced oxides. Conversely, the Song Hong (Red River) Basin, in the vicinity of Hanoi, Vietnam, appears to be another basin where a superabundance of peat (up to 5 m in thickness; BGS 1992) occurs in the area most poisoned by arsenic (Fig. 16) and gives rise to ground water compositions similar from those in the Ganges Plain (Fig. 17): ground water in both areas is rich in arsenic, iron, ammonium and phosphate, and probably for the same reason – the organic matter in the Song Hong basin is abundant enough to drive FeOOH reduction to completion. Lesser amounts of peaty sediment occur elsewhere in the Song Hong delta (Tanabe *et al.* 2003) making it likely that toxic concentrations of arsenic are widespread in the area’s ground water.

## 9. TEMPORAL TRENDS IN ARSENIC CONCENTRATIONS

### 9.1 Reasons Why the Composition of Ground Water May Change with Time

All ground waters change their composition with time: the important question is, at what rate? In the Ganges Plain, some reasons for real change are clear from the chemical stratification of the ground water: water, and hence arsenic, may move by bulk flow, both vertically and horizontally, and so redistribute arsenic. With vertical gradients in arsenic concentration of up to  $200 \mu\text{g l}^{-1} \text{ m}^{-1}$  (at FP in JAM), a small migration of the arsenic front will severely poison aquifer levels that are presently safe to exploit. Additionally, seasonal fluctuations of the water table might affect the arsenic concentration of wells screened near the water table, although this has not been observed over a monsoonal cycle elsewhere (van Geen *et al.* 2003a). In the longer term, redox reactions may deplete the store of arsenic, or FeOOH, or redox driver, in the sediments and so cause the water composition to change with time. One thing that is unlikely to cause change is a change in the rate of ground water flow. Microbial reduction of FeOOH occurs on a timescale of hours to days (*e.g.* Dowdle *et al.* 1996; Jones *et al.* 2000, Zobrist *et al.* 2000), as do in-situ redox reactions in the Ganges Plain (Harvey *et al.* 2002). Such rates are rapid in comparison to rates of ground water flow, which are typically in the range of a few centimetres per day or less (Ravenscroft 2001; Harvey *et al.* 2002), so rates of microbial reduction will be de-coupled from rates of ground-water flow.

Some reasons for apparent change with time in ground water composition include:

- 1] improving well-location as understanding of arsenic pollution improves;
- 2] poor or inconsistent techniques for sampling, sample storage, or analysis;
- 3] inappropriate purging volume;



- 4] misidentification of the well;
- 5] transcription errors.

## 9.2 Long-term Changes in the Bengal Basin

There are insufficient time-series data to demonstrate or disprove that there is a long-term change in water composition with time in the Ganges Plain. Nevertheless, tentative conclusions on long-term changes can be inferred from data on the ages and arsenic concentrations of wells documented in regional surveys (*e.g.* DPHE, 1999, 2001; van Geen *et al.* 2003a). For the shallow aquifer of Bangladesh, the proportion of wells falling above various threshold concentrations of arsenic, plotted as a function of well age (Table 6; Fig. 18), suggests that, for the first ten years of existence, the exceedance for most threshold values of arsenic increases as well-age increases, irrespective of region or threshold. A similar effect is not seen in data for sodium, (Fig. 18), an element that is largely conservative in solution, unaffected by redox transformations, and so is used as a comparator. For ages greater than ten years, the large uncertainties in the proportion of wells exceeding a given threshold, which arise as a result of the paucity of older well, makes uncertain the validity of an apparent increase in concentrations towards older ages. Similar deductions were made for a data set of 6 000 wells from the region of Araihasar (van Geen *et al.* 2003a), but were based on linear regression to highly skewed data (without log-transformation) and so may not be robust. The trend to 10 years seen in the DPHE data probably does not reflect the fact that an increasing awareness of the arsenic problem has lead drillers to site wells more carefully than before – perhaps on the basis of sediment colour. Two considerations suggest that the trends may be real. Firstly, sampling for the ‘National Survey of Arsenic Contamination’ (DPHE 1999, 2001) was completed by 1998, when the arsenic problem was not widely known about in rural areas. Secondly, there is a distinct difference in trend between redox-sensitive arsenic and the more conservative tracer sodium (Cl was not analysed for the ‘National Survey of Bangladesh’, so it could not be modelled).

In the deep aquifers of the Bengal Basin, the establishment of anoxic conditions in the deep aquifer, as a consequence of the deposition of overlying, organic-rich, Holocene aquifers, has been sufficient to mobilise some iron into groundwater in the deep aquifer (Table 3; DPHE 1999), but has been insufficient to reduce the entire pool of FeOOH, which may now act as a sorptive buffer to prevent phosphorus or arsenic from accumulating in solution. If FeOOH in the deep aquifer of the Bengal Basin does host sorbed arsenic (*i.e.* the deep aquifer has not been flushed of it – see earlier), the potential exists for downward-migrating organic matter to eventually reduce all its FeOOH and so mobilize arsenic. The data in Table 7, compiled from DPHE (2001), suggests that this is not yet happening: in the most arsenic-polluted areas of Bangladesh, deep wells have remained free of arsenic for up to 16 years.

## 9.3 Short-Term Trends in JAM.

In order to examine whether wells in the JAM area changed over the short time encompassed by our study, we sampled our wells on three separate occasions over 18 months; in February, 2002, November, 2002, and March, 2003. In our most precise data viz. electrical conductivity, calcium, magnesium, and chloride, we see some differences in water composition between samplings. Changes are small; they are best illustrated by the correlation in relative change between these determinands (Fig. 19): that between calcium and magnesium might be an analytical artefact – despite our belief in its reality – because both were measured on the same solution, with the same ICP-AES, at the same time. The determinations of chloride and electrical conductivity were made independently of calcium (chloride by ion chromatography in the laboratory, and electrical conductivity by conductivity meter in the field) so the correlation between calcium and these determinands must be real. No changes were seen in concentrations of arsenic: the analytical repeatability for arsenic analysis was around 10%, so the magnitude of any changes must be less

than this amount; our data do not rule out changes in arsenic concentration, but merely constrain the rate of change. Indeed, our piezometer profiles suggest that the depths at which ground water is contaminated will increase as organic matter moves downwards through the aquifer, consuming FeOOH, although subsequent migration of the arsenic released may be slowed by adsorption to such phases elsewhere in the aquifer.

#### 9.4 Changes Induced by Irrigation Pumping in the Bengal Basin

An important issue is whether pumping for irrigation is spreading arsenic through the shallow aquifers of the Ganges Plain, or is flushing them of arsenic by inducing additional recharge. We believe the latter is the case. This contention may be best illustrated by site FP in the JAM area (Fig. 5). The piezometer profile shows that arsenic concentration increases steeply between 31.2 and 37.0 m depth (or, given that we have only two control points, somewhere between). Given the large amount of organic matter at 29.5 m depth, the increase should occur across this unit and give higher concentrations of arsenic at 31.2 m. That it does not suggests that the entire profile has been translocated downwards by between about 2 and 9 m by abstraction of water from shallow and deep aquifers. Such movement would also have lowered arsenic concentrations above 19.2 m depth (Fig. 5) by drawing in new water to give the present profile. Water above 19.2 m depth has concentrations of calcium and sodium different to those in deeper waters, a fact that adds support to this suggestion.

Perhaps more convincingly, the depth profiles of Harvey *et al.* (2002), for groundwater in Bangladesh, show that concentrations of dissolved constituents derived from differing sources (e.g. arsenic from reduction of FeOOH; dissolved organic carbon, ammonia and methane from organic matter degradation; calcium from mineral weathering; bicarbonate from multiple sources) all increase with depth to a peak around 35-40 m depth. Such a concordance of profiles of chemically-different species can be induced only by flushing, not by reactions in the aquifer. In this context, it is interesting to compare the profiles in Munshiganj and JAM.

In JAM, arsenic concentration reach a maximum at depth in FP (Fig. 5) because of the OM-rich layer at 29.5 m depth. At AP, however (Fig. 4), the maximum is not developed strongly (if data from the upper aquitard are excluded). The progression from a 'flat' profile, similar to that seen at AP, to the 'peaked' profile seen in Munshiganj, can be achieved by depth-dependent flushing, which would lower the concentrations of all species in the upper part of the aquifer (Fig. 20). Harvey *et al.* (2002) propose or imply, instead, that the shape of many element profiles results from redox reactions that are driven by organic matter from surface sources; this is unlikely, as dissolved species move down, not up, concentration gradients, and organic matter cannot move downwards and increase in concentration as it is being consumed by reaction. The suggestion of a surface source of organic matter is also at odds with the distribution of  $^{14}\text{C}$ -ages, as discussed by van Geen *et al.* (2003b), who point out that Harvey *et al.* (2002) report measurable amounts of  $^{14}\text{C}$  to 19 m depth but not below.

A maximum in dissolved arsenic concentration around 20-40 m depth, is common across the Bengal Basin (Karim *et al.* 1997, DPHE 1999; McArthur *et al.* 2001), but not universal: for example, in Araihasar, Bangladesh, it appears to be around 15 m depth (Fig. 6 of van Geen *et al.* 2003a), whilst in the region of Sylhet, it is around 60 m and may even be bi-modal, although as a result of differential subsidence, not pumping (Ravenscroft *et al.* 2001). The explanation that shallow maxima in arsenic concentrations are caused by flushing of shallow levels in the aquifers seems reasonable because natural flow, and abstraction, particularly for irrigation, are confined to shallow depths; natural flow because of the lack of topography and the lack of natural outlets at deeper levels; irrigation flow because shallow irrigation wells are completed at shallow depths in order to minimize the cost of installation. Ground water dating by Dowling *et al.* (2002) confirms that young water may be found to depths of 30 m in the Ganges Plain. If correct, our explanation

for peaked profiles of arsenic shows that the extensive development of ground water for irrigation is reducing the arsenic problem in the ground water across the Ganges Plain.

## 10. WIDER CONSIDERATIONS

The process of FeOOH-reduction is not site specific: it can explain the arsenic problem in many sedimentary basins, both coastal and continental, because iron oxides and sorbed arsenic are ubiquitous components of clastic sediments. Whether the reduction of FeOOH will push arsenic concentrations to hazardous levels depends on how near the process goes to completion. That, in turn, is governed by the balance between the amount of FeOOH available for reaction, and the amount and reactivity of organic matter available to reduce it. Whilst concentrations of up to a few tens of microgrammes per litre of what we call kinetic-arsenic may prove common where concentrations are moderated by resorption to residual FeOOH, severe pollution by arsenic (frequent concentrations of arsenic  $> 100 \mu\text{g l}^{-1}$ ) require the accumulation of organic matter in amounts sufficient to exhaust the store of FeOOH in sediments that are in hydraulic continuity with aquifer sands. This condition is met most commonly on the margins of buried peat basins, where organic matter accumulates in low percentage-abundance, either in confining units that are moderately permeable, or in the aquifer sands themselves, or where significant loadings are contributed by human or animal activity.

As proposed by P. Ravenscroft, as senior author of DPHE (1999), and by Ahmed and Ravenscroft (2000) and Ravenscroft *et al.* (2001), and since repeated by Smedley and Kinniburgh (2002), the global rise in sea-level between 18 and 6 Ka, created settings worldwide for arsenic-polluted aquifers to form. The large volume of accommodation space that resulted is now filled with recent sediments. The rates of sea level rise and sediment supply have been the primary controls on wetland formation, where organic-rich muds and alluvial or deltaic sands are closely juxtaposed. Pollution of ground water by arsenic will therefore be most prevalent in depositional areas where climate was hot and wet during the climax of deposition of nearshore sediment around 4 - 8 ka, and where chemical weathering in the upper catchment was limited. A set of globally applicable parameters – the depth of pre-Holocene incision, the relative rates of sea level rise and alluvial aggradation, the Holocene climatic record, and the geology of the upper catchment – therefore provide a general model for predicting the possible occurrence of arsenic in coastal alluvial basins. Inland basins lack the drainage control imposed by global sea-level, so inland basins will be subject to local base-level controls and application of the outline model to such areas may be difficult. In a global context, the physical and demographic characteristics of the Bengal Basin represent an extreme, in which the extreme topography of the hinterland, its weathering under extremes of climate, and its crystalline geology, have conspired to exacerbate the problem by minimising chemical weathering and production of FeOOH. Other areas that might be expected to suffer from arsenic pollution, although perhaps to a lesser degree than in the Bengal Basin, include the deltas of tropical rivers such as the Mekong, Irrawaddy, and Chao Phraya rivers, and the coastal plains of Java and Sumatra.

## 11. CONCLUSIONS

In the Ganges Plain, arsenic is released to solution by reductive dissolution of FeOOH and release of its sorbed arsenic to ground water. In our study area near Barasat, and, by implication, elsewhere in the Bengal Basin and worldwide in alluvial aquifers, the reduction is driven by natural organic-matter buried in sediments. The organic matter exists in moderate amounts within

the upper confining units of the aquifers and in the aquifer sands, either as dispersed OM or as discrete organic-rich units. In JAM, the organic matter accumulated in peat basins; the portion that drives reduction in the aquifer is that which accumulated on the margins of the basin where the sediments are sufficiently permeable to allow infiltration to the aquifer of the soluble organic products of fermentative degradation of the organic matter. Within the JAM area, which is typical of much of the southern Ganges Plain, surface sources of organic matter do not contribute to the reduction of FeOOH and so do not result in ground water containing high concentrations of arsenic. In areas of the Ganges Plain where pit latrines penetrate the upper confining layer, sewage, deposited in hydraulic continuity with the aquifer, will promote additional reduction of FeOOH and add to arsenic pollution. Unless populations reach an urban density, however, this process will not exacerbate the regional pollution by arsenic, but will operate at the scale of individual wells.

Where the reduction of FeOOH goes to completion, concentrations of arsenic often exceed  $100 \mu\text{g l}^{-1}$ . Where reduction of FeOOH is incomplete, concentrations of kinetic arsenic in solution are moderated (to  $< 100 \mu\text{g l}^{-1}$ ) by resorption to residual FeOOH. The extent of arsenic mobilisation will be controlled by the balance between the quantity and biodegradability of organic matter, and the size of the FeOOH buffer available to sorb arsenic. Reduction of FeOOH in the Ganges Plain commonly goes to completion because the sediments contain abundant natural organic matter to drive reduction but little FeOOH, owing to the immaturity of the sediment, which is produced and transported rapidly from a crystalline Himalayan source to its place of accumulation in the anoxic environment of the Bengal Basin.

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- Fig. 6. Water levels in piezometers at sites DP, AP, and FP, in metres relative to an arbitrary datum in March, 2003. At each site, the uppermost piezometer was completed close to the base of the upper confining unit. The higher head in the upper confining unit at Site DP arises from the impermeable clay unit that locally caps the aquifer at this site. At FP and AP, the aquifer sands are capped by more permeable silts.
- Fig. 7. Map of the distribution of As, Fe, Mn and SO<sub>4</sub> in JAM wells. Symbols as on each figure. Wells near piezometer DP are rich in manganese and lack arsenic: wells in northwestern JAM are rich in arsenic and iron. For a discussion of why, see text.
- Fig. 8. Relation in March, 2003, in JAM wells between (a) As and Mn (b) As and SO<sub>4</sub>, (c) As and Fe (d) As and PO<sub>4</sub> (e) Fe and PO<sub>4</sub>, (f) Fe and SO<sub>4</sub>. Wells are categorized using As/Fe and arsenic concentration as proxies for depth. Open squares are wells with > 32 μg l<sup>-1</sup> of arsenic and low As/Fe values; filled circles are wells with > 32 μg l<sup>-1</sup> of arsenic and high As/Fe values; small open circles are wells containing < 16 μg l<sup>-1</sup> of arsenic. See text for an explanation of the relation of these groupings to well depth.
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Towards the basin centre, permeability decreases; away from the basin, the abundance of organic matter decreases: in both cases, pollution by As decreases.

- Fig. 15. Detailed profiles of water composition in the basal aquifer at Site AP, showing the invariance in pH and in the concentrations of  $\text{HCO}_3^-$ , and  $\text{H}_4\text{SiO}_4$ , in contrast with the change in concentration of dissolved As,  $\text{PO}_4$  and Fe.
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