

P. Ravenscroft^{1,2}, J.M. McArthur^{3*} and B.A. Hoque^{4,5} (2001). Geochemical and Palaeohydrological Controls on Pollution of Groundwater by Arsenic. *In: Arsenic Exposure and Health Effects IV*. W.R. Chappell, C.O. Abernathy & R. Calderon (Eds), p 53-78, Elsevier Science Ltd. Oxford.

¹*Mott MacDonald International, 122 Gulshan Avenue, Dhaka 1212, Bangladesh.*

²*Present address, Arcadis Geraghty & Miller International Inc., Conqueror House, Vision Park, Histon Cambridge CB4 9ZR.*

³*Geological Sciences, University College London, Gower Street, London WC1E 6BT, UK.*

⁴*ICDDR,B, Dhaka, Bangladesh.*

⁵*Present address, World Bank, Dhaka, Bangladesh.*

*Corresponding author: j.mcarthur@ucl.ac.uk
www.es.ucl.ac.uk/research/lag/as/

ABSTRACT

Reduction of iron oxyhydroxide (FeOOH) and release of its sorbed arsenic load to solution is an important mechanism by which groundwater worldwide becomes polluted with arsenic. In the Bengal Basin of Bangladesh and West Bengal (India), it is the main mechanism by which arsenic pollutes groundwater. Arsenic pollution does not arise from oxidation of sedimentary sulfides nor from ion-exchange with phosphorus derived from fertilizer (or other sources). The concentration of arsenic in the sediments of the Bengal Basin is not exceptional and the occurrence of reducing conditions alone is insufficient to explain the extreme degree and extent of arsenic pollution. Extreme pollution by arsenic occurs because biodegradation of buried peat deposits drives extreme degrees of FeOOH reduction and supplies high concentrations of arsenic to groundwater (hundreds of $\mu\text{g l}^{-1}$). Sources of organic matter other than peat are neither reactive enough nor abundant enough to generate the amount and degree of reduction necessary to cause such severe arsenic pollution but may account for pervasive low-level contamination ($< 50 \mu\text{g l}^{-1}$). The distribution of known peat basins, and their ages, correlates to some degree with the surface distribution and depth profiles of arsenic. The distribution of peat and arsenic can be related to the Late Pleistocene and Holocene evolution of the Bengal basin. Because this evolution is controlled largely by climatic fluctuations and sea-level changes, a general model emerges for predicting the occurrence of groundwater that is naturally polluted by arsenic.

1. INTRODUCTION

Throughout this article the term contamination means an unusual concentration of something whilst the term pollution means an unusual concentration that leads to environmental harm. Arsenic pollution of groundwater in the Bengal Basin was known about in the late 1980s (*Guha Mazumder et al.* 1988, *PHED* 1991) and, although overlooked by a later survey (*BGS* 1992), is now known to be one of the World's worst disasters affecting humans. At least 28 million people currently drink water containing more than $50 \mu\text{g/l}$ of arsenic (the current Bangladesh drinking water standard), and many more consume water with $> 10 \mu\text{g/l}$ of arsenic (*Dhar et al.* 1997; *Ullah* 1998; *Mandal et al.* 1998; *DPHE* 1999, 2000; <http://bicn.com/acic/>, 28/10/00). The human consequence of the pollution has been described as the worst mass poisoning of a population in history (*Smith et al.* 2000).

Understanding the source of such severe arsenic pollution has a number of important benefits. Firstly, it helps in locating polluted aquifers and in predicting the future trends of arsenic in groundwater. Secondly, it is of great significance in formulating agricultural policy. For example, a common misconception is that pumping of groundwater for irrigation has caused arsenic pollution, with one consequence being a call for a ban on tubewell irrigation in Bangladesh. Yet irrigation has been the principal factor behind Bangladesh attaining virtual self-sufficiency in foodgrain production, and hence a great diminution in the incidence of famine. A ban on groundwater irrigation, unjustified by rigorous scientific compulsion, would have severe adverse consequences for food security, rural livelihoods and the economic future of the poor of Bangladesh. We show that irrigation has no causal relation with arsenic pollution. We also show that

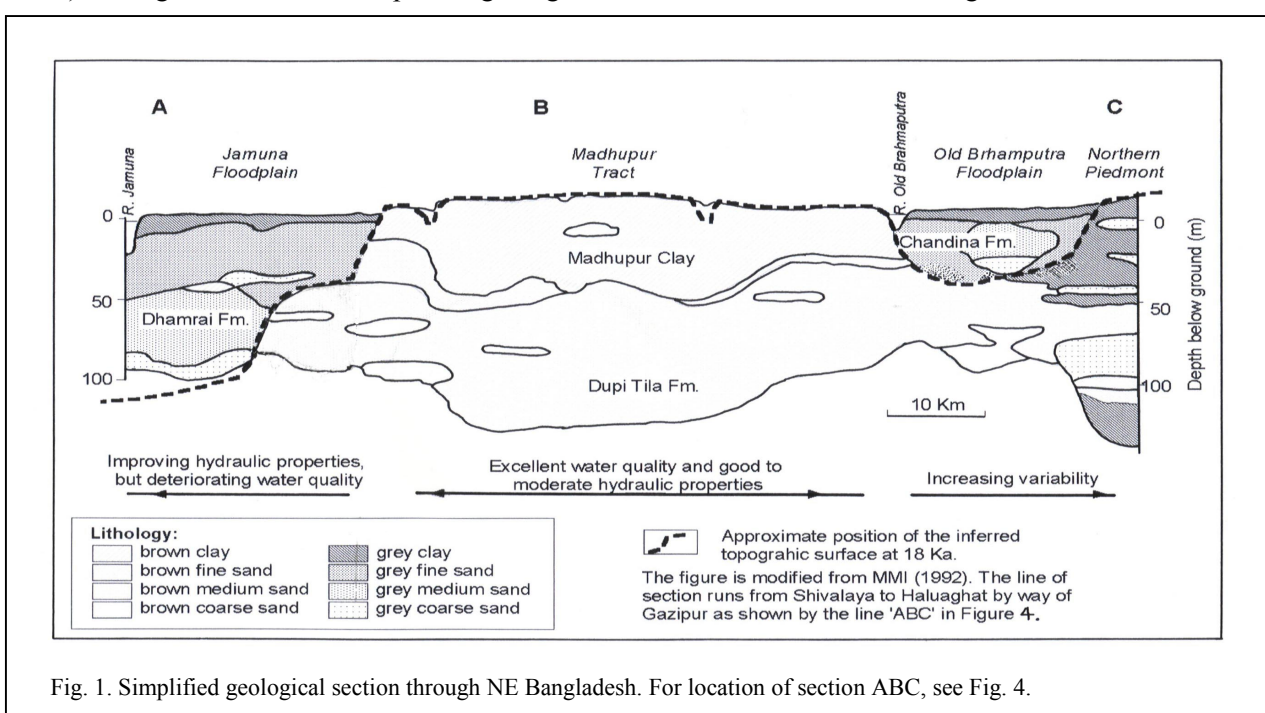
arsenic contamination is not caused by oxidation of sulfide minerals as water tables are lowered by pumping (Mallick and Rajagopal, 1996; Mandal *et al.* 1998; Roy Chowdhury *et al.* 1999). We dismiss, giving reasons, the suggestion (Acharyya *et al.* 2000) that arsenic pollution is caused by ion-exchange by phosphate from fertilizers (or any other source of phosphorus).

We confirm previous suggestions (Bhattacharya *et al.* 1997; Nickson *et al.* 1998, 2000; McArthur *et al.* 2001) that arsenic pollution in the Bengal Basin is a natural process whereby arsenic is released during reductive dissolution of iron oxyhydroxides, a process that also reduces the sorbed arsenate to arsenite (Zobrist *et al.* 2000). The reduction hypothesis (Nickson *et al.* 1998, 2000; McArthur *et al.* 2001) assigns great importance to the role of organic matter, in particular, peaty sediments, in generating anoxia in groundwater. This paper give evidence that peat is the redox driver for reduction of FeOOH and then examines the sedimentological evidence that supports the proposition that the distribution of pollution by arsenic reflects the distribution of buried deposits of peat. In doing the above we make use of our own data, data from a survey of bacterial contamination and ammonium by Hoque (1998) and data from DPHE (1999, 2000) which are available from <http://www.bgs.ac.uk/arsenic/Bangladesh>.

2. HYDROGEOLOGY OF THE BENGAL BASIN

The Bengal Basin is one of the World's largest sedimentary basins and has accumulated a great thickness of Tertiary and Quaternary clastic sediments that were transported to the area by the Ganges-Brahmaputra-Meghna river system (Morgan and McIntire, 1959). Bangladesh occupies most of the Bengal Basin and comprises mainly alluvial and deltaic floodplains except for the small uplifted blocks of the Barind and Madhupur Tracts in the central and north-western parts of the country. On the east, Bangladesh is bounded by the Chittagong Hill Tracts and in the northeast by the Shillong plateau. The sedimentary sequence typically comprises multiple fining-upwards successions of sand, silt and clay with occasional layers of gravel at the base.

Recent alluvium forms prolific shallow aquifers under water table or leaky conditions and, beneath the uplifted Barind and Madhupur blocks, the Plio-Pleistocene Dupi Tila Formation forms an important leaky-to-confined aquifer. Both are used for irrigation and water supply. The transmissivity of the alluvial aquifers is typically in the range of 1 000 to 5 000 m²/d, and is highest beneath the alluvial floodplains. The distribution of aquifer and water properties has been strongly influenced by the pattern of river incision and infilling that occurred in response to glacial-eustatic sea level changes in the Quaternary (Ravenscroft 2001). In Fig. 1 we show a simplified geological section across north-east Bangladesh that illustrates the



lateral and vertical pattern of Holocene valley-fill and Pleistocene interfluvial deposits. The characteristically brown Madhupur Clay and Dupi Tila sands are the remnants of uplifted blocks that existed during sea-level low stands. Monsur (1995) deduced an early Pleistocene age for the Madhupur Clay, while Whitney *et al.* (1999) infer ages of 25,000 and more than 125,000 years for the surfaces of the Barind and Madhupur Tracts respectively. The valley-fill sediments are represented by the Dhamrai and Chandina Formations. Deposits of the terminal Pleistocene-Holocene transgression reach a thickness of at least 90 m in the central Jamuna valley (JICA, 1976). However, dating of wood samples by BGS (1992) points to the presence of stepped terraces (probably Middle or Upper Pleistocene) between the central valley and the Madhupur Tract.

Sediments of the major interfluves (or *doabs* as defined by Singh *et al.* 1999) are brown, oxidised and highly weathered with a surface clay cover. As aquifers, they are generally confined, having low vertical and horizontal permeability and specific yields, but they contain water of excellent quality; it is typically a sodium bicarbonate type, with EC between 200 and 500 $\mu\text{S cm}^{-1}$, low iron ($< 1 \text{ mg l}^{-1}$), and with arsenic concentrations mostly less than 10 $\mu\text{g l}^{-1}$. The Holocene sediments are typically grey, unweathered, and often contain abundant organic matter. Although the Holocene aquifers have high permeability (40 - 80 m d^{-1}), specific yield and potential recharge rates, they have poorer water quality, the water being fresh but more mineralized (EC 500 - 1 200 $\mu\text{S cm}^{-1}$) and contain higher proportions of calcium and magnesium. The waters are anoxic, high in iron, manganese and bicarbonate but mostly low in nitrate and sulfate; many are sulfidic and/or methanogenic (Ahmed *et al.* 1998; Nickson *et al.* 1998, 2000; DPHE 1999; Gavrieli *et al.* 2000).

The piezometric surface is within a few metres of the surface for most of the year. In areas of intensive irrigation, water levels fall to between 5 and 15 metres below ground for two to three months but return to the ground surface in low lying areas during the monsoon, when the aquifer is full. Only in Dhaka City, in response to intensive and continuously increasing abstraction, has the water table been permanently lowered and an original confined condition has become unconfined. Outside Dhaka City, gross annual abstraction ranges from a few tens of millimeters a year where groundwater is used only for drinking to over 500 mm a year in areas of intensive tubewell irrigation.

3. ARSENIC POLLUTION IN BANGLADESH

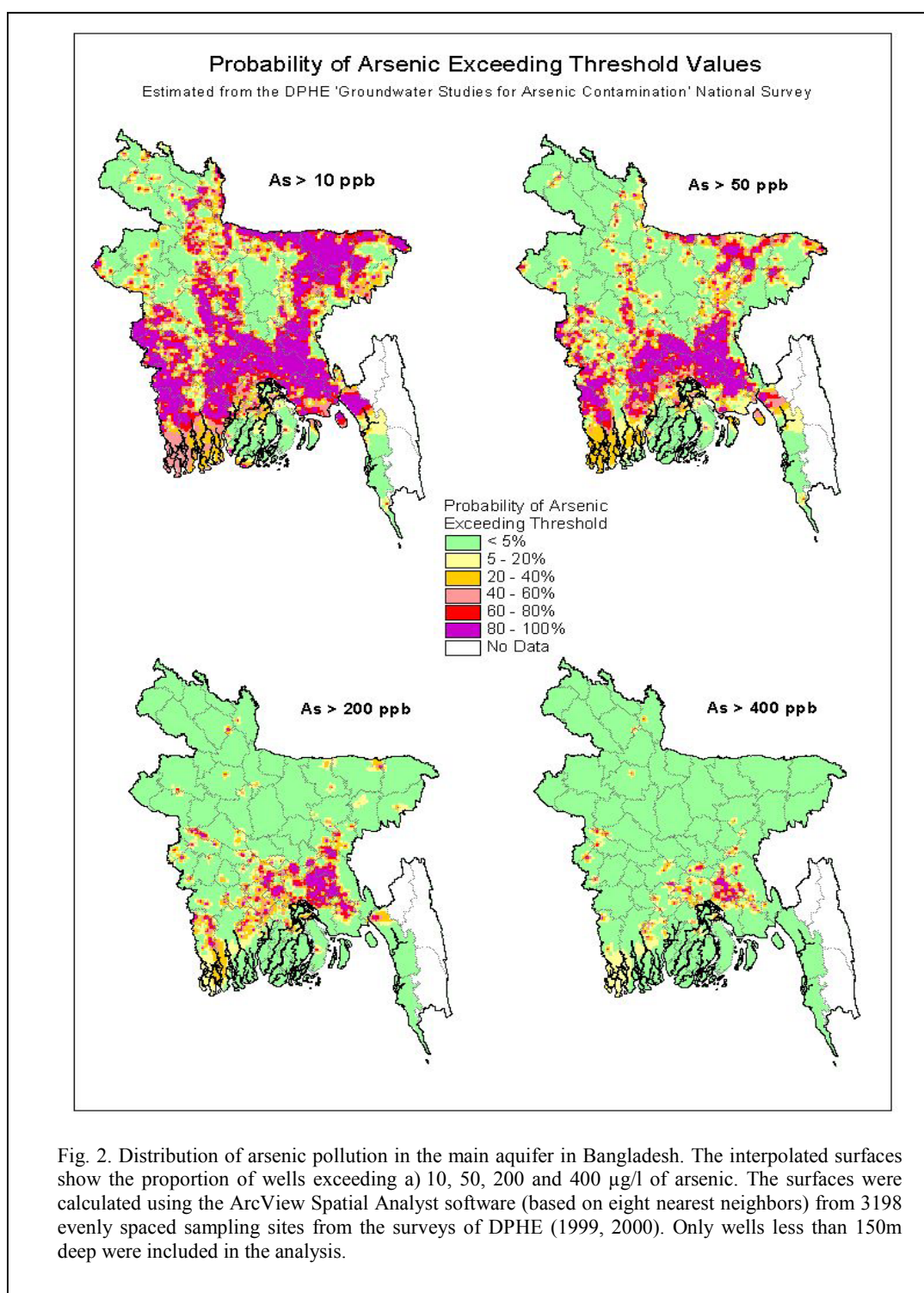
Geographical Variation

The probability of arsenic exceeding 50 $\mu\text{g/l}$ and 250 $\mu\text{g/l}$ in the upper 150 m of the aquifer system is strongly correlated with surface geology, both in terms of age and provenance (DPHE 1999). The distribution of arsenic polluted groundwater beneath the floodplains of the Ganges, Brahmaputra and Meghna rivers is shown in Fig. 2, which is based on 3 198 wells of depth $< 150 \text{ m}$ (mostly $< 100 \text{ m}$). Summary statistics from the DPHE surveys are given in Table 1.

Table 1. Summary statistics, from National Arsenic Survey (DPHE 1999, 2000).

Arsenic $\mu\text{g/l}$	No.	%	% > Lower Bound
≤ 10	2042	58	-
10-50	611	17	42
50-250	639	18	75
250-500	178	5.0	93
> 500	64	1.8	98
All	3534	100.0	-

The distribution of arsenic pollution shown in this Fig. 2 differs little from that shown in Fig. 1 of *McArthur et al.* (2001) which was based on 19 471 DPHE field and laboratory data. The comparison indicates that the smaller sample size of the former is sufficient to reflect the regional (but not local) distribution of arsenic in groundwater. Except in the coastal region, the vast majority of wells are hand-pumped with short screens (mostly 3 to 6 metres long) set at a level as shallow as practical in the aquifer. In the Lower Pleistocene and older aquifers (Barind, Madhupur and Chittagong Hill Tracts), arsenic is mostly below detection limits (around a few microgammes per litre). Elsewhere, although landforms constituting the floodplains of the three major river systems differ at all scales (including village and sub-regional), aquifers underlying the Meghna floodplains are polluted most and those under the Brahmaputra floodplains are polluted least: it is significant that arsenic pollution occurs in the catchments of all three rivers and that the intensity of arsenic pollution increases towards the lower part of the basin (Fig. 2; Fig 1 of *McArthur et al.* 2000).



Variations with Depth

Arsenic concentration is strongly dependent on depth (Karim *et al.* 1997, DPHE 1999; Fig. 3). The highest concentrations of arsenic, and the highest probability of exceeding thresholds for arsenic, most often occur in wells screened between 20 and 60 m (Fig. 3) but the precise depth of the maximum varies between regions and the sharpness of the concentration peak differs from place to place. In Dhaka Division (Fig. 3c),

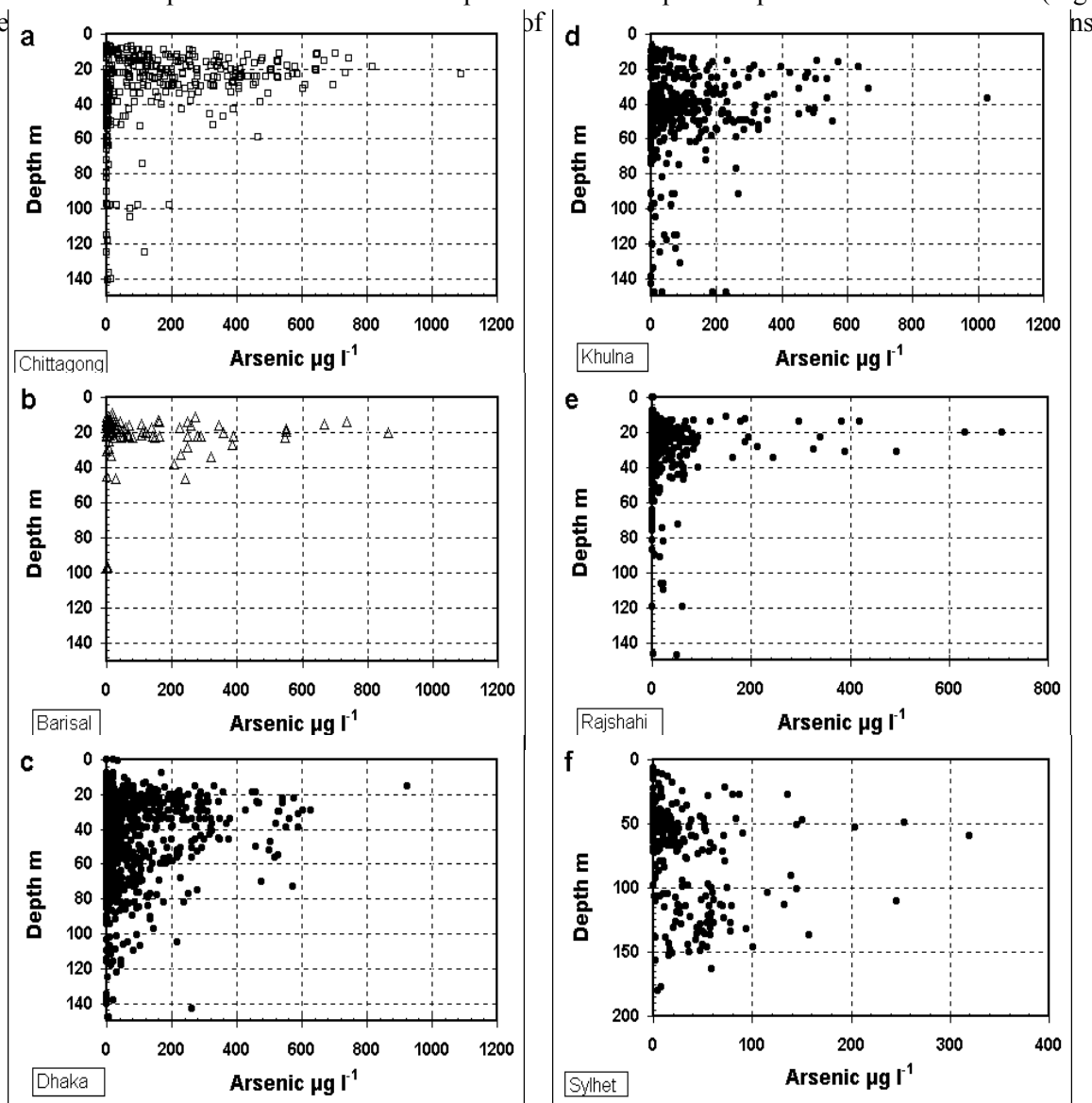


Fig. 3. Distribution of arsenic with depth in the six Divisions of Bangladesh. Depths >150 m are not plotted for a-e as wells >150 m deep seldom exceed $50\mu\text{g l}^{-1}$. Note different scales for e and f.

peak at both 60 and 120 m. The depth distributions in Fig. 3 show to be fallacious the belief that drilling deeper than 100 m provides arsenic free water; it will do so in some parts of Bangladesh, but not, for example, in the region of the Sylhet Basin. A sharp upper limit to high concentrations of arsenic appears to occur at about 10-15 m depth; few data are available for wells in the depth range 0-10 m, so this may be an artefact of data distribution. That it is not is suggested by the fact that dug wells, which are mostly much less than 10 m deep, are rarely polluted with arsenic (Chakraborty 2001), which we presume is because they are usually oxic and so have avoided arsenic pollution from FeOOH reduction. Below 200 m, arsenic concentrations rarely exceed a few micrograms per litre (Frisbie *et al.* 1999; DPHE 1999; Fig. 3).

4. THEORIES OF ARSENIC MOBILIZATION

Three mechanisms might explain arsenic pollution of groundwater in the Bengal Basin, viz:

- 1) arsenic is released by oxidation of arsenic-bearing pyrite in the alluvial sediments (*Mallick and Rajagopal 1996; Mandal et al. 1998*);
- 2) arsenic anions sorbed to aquifer minerals are displaced into solution by competitive exchange of phosphate anions sourced from over-application of fertilizer to surface soils (*Acharyya et al. 2000*);
- 3) naturally-occurring arsenic that is sorbed to iron oxyhydroxides (FeOOH) is released when the iron oxyhydroxide is reduced as anoxic conditions develop during sediment burial (*Bhattacharya et al. 1997; Nickson et al. 1998, 2000; McArthur et al. 2001*).

1: Pyrite Oxidation and Irrigation Drawdown

We reject oxidation of arsenical pyrite as a mechanism for arsenic pollution in Bangladesh, even though trace pyrite is present in aquifer sediments (*PHED 1991; AAN 1999; Nickson et al. 1998, 2000; McArthur et al. 2001*). Oxidation of pyrite is envisaged to happen as irrigation draws down the water table allowing

oxygen into previously anoxic aquifer sediments. A relation between the distribution of arsenic pollution (Fig. 2) and that of irrigation (Fig. 4) is therefore be expected, yet a comparison of Figs. 2 and 4 shows they bear no relation to each other: indeed, the distributions appear antipathetic. This geographical evidence does not support the existence of a causal link between arsenic pollution and tubewell irrigation. The distribution of maximum dry-season water table lowering is similar to that shown in Fig. 4 and is also antipathetic to the pattern of arsenic pollution.

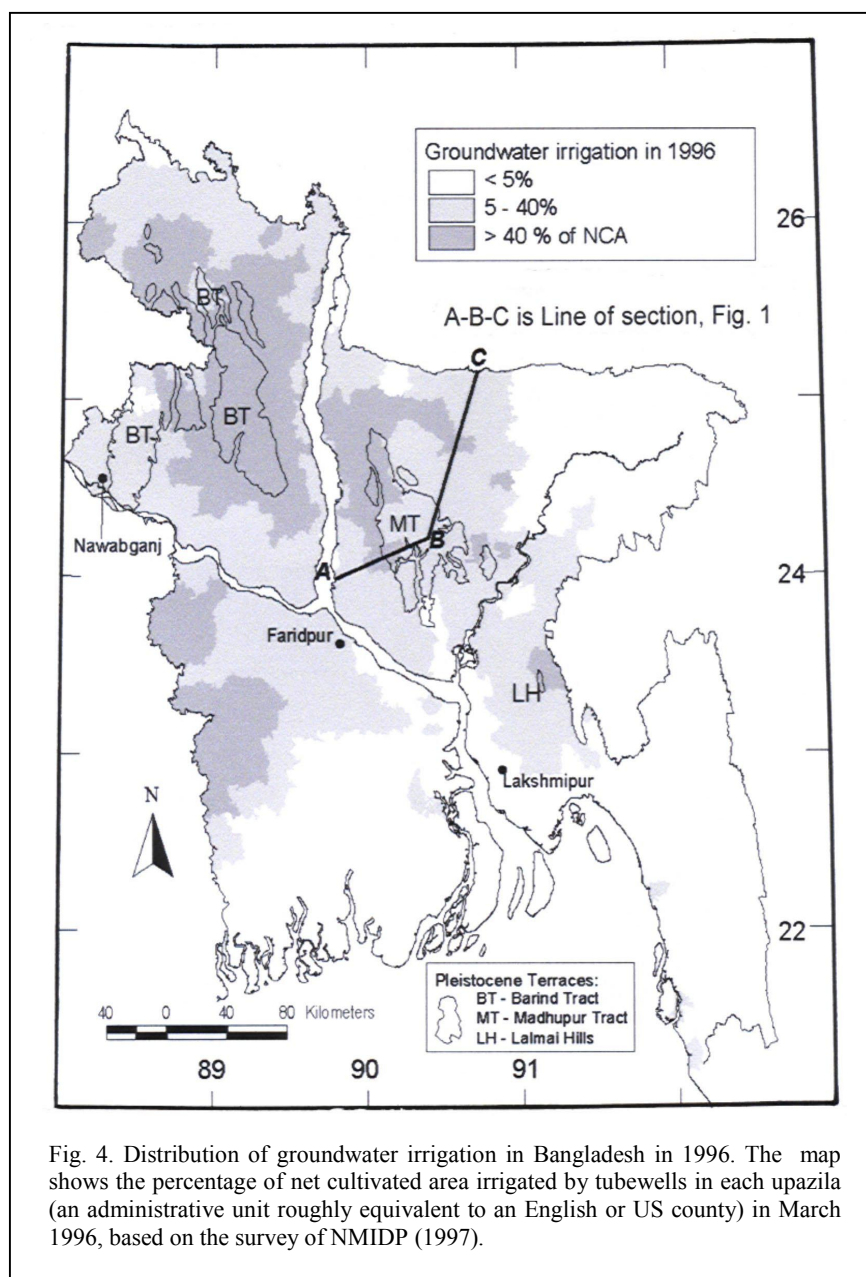
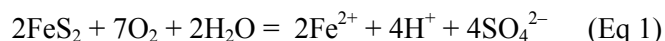


Fig. 4. Distribution of groundwater irrigation in Bangladesh in 1996. The map shows the percentage of net cultivated area irrigated by tubewells in each upazila (an administrative unit roughly equivalent to an English or US county) in March 1996, based on the survey of NMIDP (1997).

Other reasons for rejecting pyrite oxidation as a mechanism are as follows. The sediments contain too little arsenical pyrite for this mechanism to be important. Measured sulfur concentrations in aquifer sediments represent both pyritic and organic sulfur but allow upper limits to be placed on pyrite abundance of 0.3% [*Nickson et al. 2000*], 0.02% [*AAN 1999*], 0.1% [*J.M. McArthur unpublished*] and 0.06% [*DPHE 1999*]. Were arsenic to be released by partial-oxidation of arsenical pyrite,

Bangladesh groundwaters, which are anoxic, would have an iron/sulfate molar ratio of 0.5 from the stoichiometry of the reaction :



In reality, iron and sulfate are mutually exclusive in solution (Fig. 5), as are arsenic and sulfate (Fig. 5); arsenic concentrations $> 50 \mu\text{g l}^{-1}$ occur only where sulfate concentrations are $< 30 \text{mg l}^{-1}$. If oxidation were complete and FeOOH was produced, rather the Fe^{2+} that would form by partial oxidation, the arsenic would be sorbed to the this FeOOH [Mok and Wai 1994; Savage *et al.*, 2000]. Finally, arsenic pollution is uncommon in hand-dug wells [Chakraborty *et al.* 2001] which are shallowest and most exposed to atmospheric oxygen and so would be most polluted were arsenic derived from pyrite by oxidation

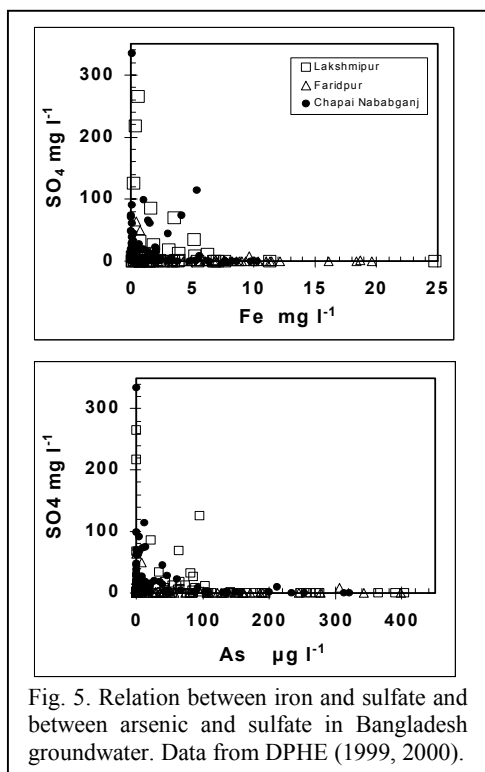


Fig. 5. Relation between iron and sulfate and between arsenic and sulfate in Bangladesh groundwater. Data from DPHE (1999, 2000).

Pyrite forms during early burial, either by reaction of dissolved hydrogen sulfide (from sulfate reduction) with solid FeOOH or reaction of dissolved Fe^{2+} with dissolved sulfide ions. In the former case, arsenic sorbed on FeOOH will be incorporated into the resulting pyrite. In the latter case, as iron reduction precedes sulfate reduction in the sequence of diagenetic reactions, the arsenic released by FeOOH reduction will be sequestered from solution by pyrite forming from later sulfate reduction. The presence of trace pyrite in the sediments shows that it has not been oxidised and so is not a source of arsenic in Bangladesh groundwater. Beneath Samta village (Fig. 6), concentrations of arsenic and iron co-vary strongly and show a maximum within a layer of peat at about 10 m depth that acts as a reducing locus for pyrite formation; this peat layer is also a locus of arsenic removal from groundwater as arsenic is incorporated into diagenetic pyrite. Under the anoxic conditions of the groundwater, this arsenic is immobilized in pyrite and neither the pyrite in the peat nor the peat itself is a source of arsenic to groundwater.

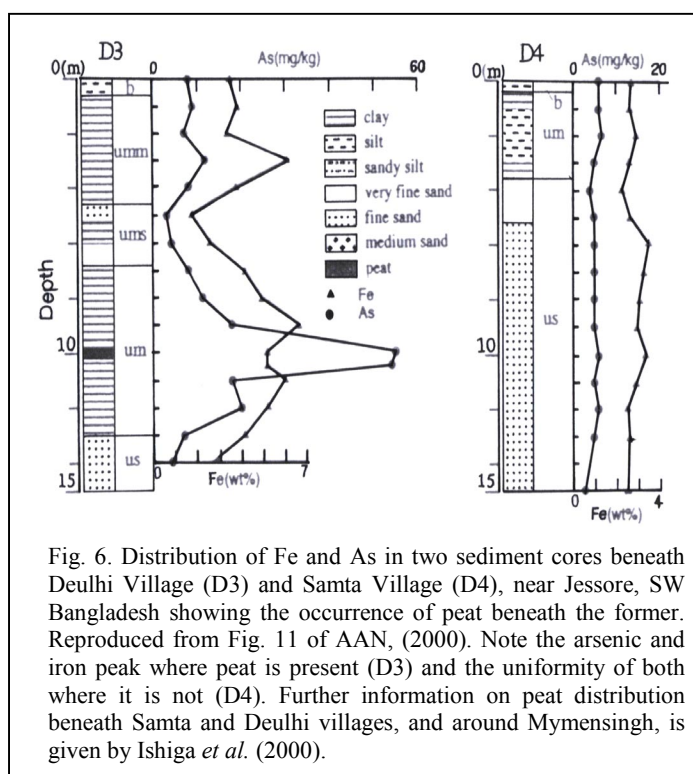


Fig. 6. Distribution of Fe and As in two sediment cores beneath Deulhi Village (D3) and Samta Village (D4), near Jessore, SW Bangladesh showing the occurrence of peat beneath the former. Reproduced from Fig. 11 of AAN, (2000). Note the arsenic and iron peak where peat is present (D3) and the uniformity of both where it is not (D4). Further information on peat distribution beneath Samta and Deulhi villages, and around Mymensingh, is given by Ishiga *et al.* (2000).

2: *Competitive Exchange with Fertilizer-Phosphate*
The fact that the use of phosphate fertilizer in Bangladesh has increased greatly over the past 15 years has led to suggestions (*e.g.* Acharyya *et al.* 2000) that the arsenic pollution may result, at least in part, from the displacement from FeOOH of sorbed arsenic as a result of competitive (anion) exchange by phosphate leached from soils after excessive use of phosphate fertilizer. We reject this idea. The use of phosphate fertilizer in Bangladesh is widespread (Table 2) but amounts used are not high by international standards.

Table 2. Figures typical of fertilizer use in Bangladesh. TSP = triple-superphosphate; MOP = muriate of potash. Source, National Water Management Plan project of Bangladesh.

Crop	Fertilizer (Kg / ha)		
	Urea (46% N)	TSP (46% P ₂ O ₅)	MOP (50% K ₂ O)
HYV T. Aus (irri.)	80	40	10
HYV Boro	170	70	25
HYV T. Aman (irri.)	30	110	50
HYV T. Aman (rainfed)	110	50	15

There are extensive areas of the country where groundwater is essentially free of both arsenic and phosphorus (Figs. 2 and 7) and it is in these areas that irrigation is most intense and application of fertilizer might be expected to be highest. This argument alone seems to us sufficient to reject any link between fertilizer and arsenic. Another such argument is that waters attain a bicarbonate concentration of at least 200 mg l⁻¹ before phosphorus, arsenic, or iron, are found in significant amounts (*McArthur et al.* 2001). Waters lowest in bicarbonate are the youngest and least evolved, but they would contain most phosphorus (and so arsenic), were phosphorus supplied from surface application of fertilizer.

The fact that phosphorus in groundwater cannot contribute much to arsenic pollution is shown by the experimental desorption by phosphate of arsenic sorbed to mineral surfaces (*Manning and Goldberg* 1997). These authors showed that P/As mole partition ratios for desorption of arsenic by phosphate were around 5 000. Given this ratio, no more than 2 µg l⁻¹ of arsenic would be desorbed by a phosphorus (as P) concentration in groundwater of 5 mg l⁻¹, the approximate upper limit for Bangladesh groundwaters. Add the fact that ageing increases arsenic retention on FeOOH and it can be seen that arsenic pollution by competitive exchange with phosphorus will be negligible, whatever the sources of phosphorus.

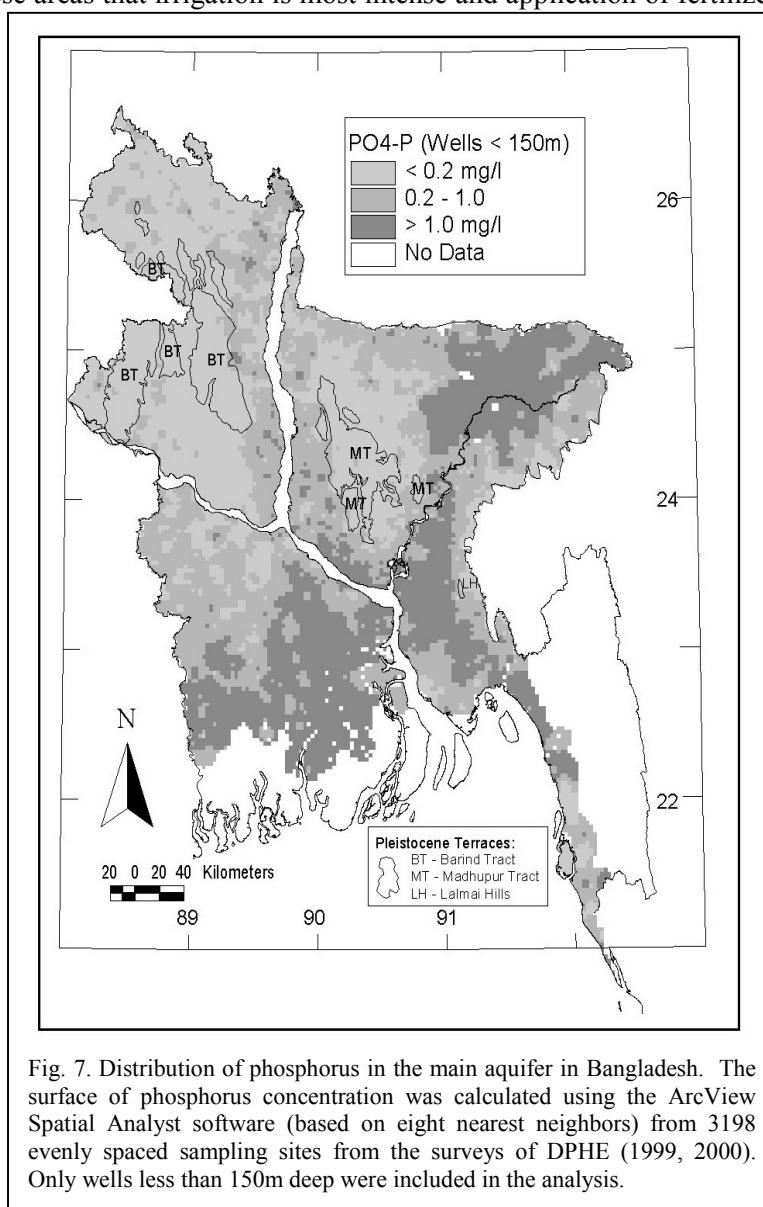


Fig. 7. Distribution of phosphorus in the main aquifer in Bangladesh. The surface of phosphorus concentration was calculated using the ArcView Spatial Analyst software (based on eight nearest neighbors) from 3198 evenly spaced sampling sites from the surveys of DPHE (1999, 2000). Only wells less than 150m deep were included in the analysis.

A final argument concerns the fact that phosphate fertilizer contains uranium, so this element may be used as a tracer for fertilizer phosphate. In Bangladesh groundwater, concentrations of uranium are mostly very low; where uranium is found in high concentrations, the concentrations of phosphorus are low to zero. The distribution of uranium is therefore de-coupled from the phosphorus distribution probably because, on infiltration, fertilizer phosphorus is taken up by plants (as intended) whilst fertilizer uranium, which is mobile in the oxic environment, moves downwards to the water table and contaminates some wells.

Furthermore, uranium is not found in wells greater than 41 metres deep (Fig. 8), whilst phosphorus concentrations increase with depth in both Faridpur and Lakshmipur (not shown, but based on DPHE 2000). These arguments further reinforce our case that phosphorus from fertilizer has no significant role in causing arsenic pollution. Nevertheless, concentrations of uranium are high (Fig. 8) in (mostly oxic) shallow concrete ring wells in Nawabganj, viz. BTS428 (47 $\mu\text{g l}^{-1}$ U) and BTS438 (41 $\mu\text{g l}^{-1}$ U), both 9m; BTS347 (20 $\mu\text{g l}^{-1}$ U, 8m deep); BTS 357 (U 8 $\mu\text{g l}^{-1}$ and 4m deep) and BTS 355 (4 $\mu\text{g l}^{-1}$, 9m deep) and we cannot discount entirely the possibility that some uranium is leached from the concrete (although not all wells with high uranium are concrete ring wells).

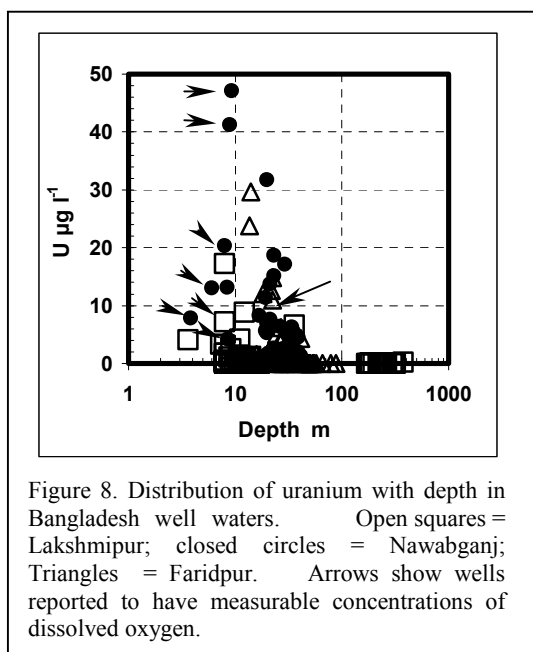
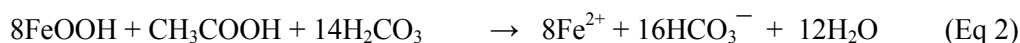


Figure 8. Distribution of uranium with depth in Bangladesh well waters. Open squares = Lakshmipur; closed circles = Nawabganj; Triangles = Faridpur. Arrows show wells reported to have measurable concentrations of dissolved oxygen.

that may influence policy and so benefit the farmers of Bangladesh.

3: Reduction of FeOOH

Reduction of FeOOH is common in nature and has been invoked previously to explain the presence of arsenic in anoxic surface waters (Aggett and O'Brien 1985; Cullen and Reimer 1989; Belzile and Tessier 1990; Ahmann et al. 1997) and anoxic groundwaters (Gulens et al. 1979; Matisoff et al. 1982; Korte 1991; Korte and Fernando 1991; Bhattacharya et al. 1997; Nickson et al. 1998, 2000; McArthur et al. 2001; refs. therein). Reduction of FeOOH (Equation 2) is a microbial process



that is driven by microbial metabolism of organic matter, particularly acetate (see Nealson 1997; Lovley 1997; Banfield et al. 1998; Chapelle 2000; Lovley and Anderson 2000) and is accompanied by microbial reduction of arsenate to arsenite (Zobrist et al. 2000, but also Ahmann et al. 1997; Dowdle et al. 1996; Stolz and Oremland 1999). That reduction of FeOOH is common and intense in the aquifers of the Bengal Basin is shown by high concentrations of dissolved iron ($\leq 24.8 \text{ mg l}^{-1}$, DPHE 1999; $\leq 29.2 \text{ mg l}^{-1}$, Nickson et al. 2000; $\leq 80 \text{ mg l}^{-1}$, Safiullah 1998); that it is accompanied by reduction of As(V) to As(III) is shown by the fact that dissolved arsenic is present overwhelmingly as arsenite (Gavrieli et al. 2000). The finding of significant amounts of arsenate in Bangladesh groundwater (DPHE 1999, 2000) is an artefact of the storage of iron-rich waters before analysis, a procedure known not to preserve arsenic speciation (Cherry et al. 1979; Korte and Fernando 1991; Borho and Wilderer 1997; Hall et al. 1999; Volke and Merkel 1999; G. Cutter, pers. comm. 2000). Given that microbial metabolism of organic matter drives reduction of iron and arsenic, the generation of some organic arsenic species might be expected. Using the method of Wangkarn and Pergantis (2000), we have analysed for MMAA and DMAA in water from 13 wells in Faridpur, sampling in both February 2000 and March 2001. In no sample was either above the detection limit of 2 ppb.

The spatial distribution of phosphorus in well-water closely parallels that of arsenic (cf. Fig. 2 and Fig. 7), although the well-by-well correlation of arsenic and phosphorus concentrations is modest. This similarity of distributions points to a common diagenetic origin for arsenic and phosphorus. Both elements form anions that sorb strongly to iron oxyhydroxide and their joint release during reduction of FeOOH probably contributes to their similar geographical distributions.

An invocation of FeOOH reduction to explain arsenic pollution needs to address why some groundwaters in Bangladesh are high in iron and low in arsenic and others are low in both. Arsenic pollution and iron are

absent from groundwaters in aquifers of Lower Pleistocene and older age, beneath the Madhupur Tract and the Barind Tract, because these aquifers are oxic and, particularly where iron has been recrystallized as more stable phases such as hematite (BADC, 1982), reductive dissolution of iron oxyhydroxides does not occur in them. In coastal Lakshmipur, where both shallow (<40 m) and deep (>130 m) aquifers are anoxic and contain dissolved iron, only the shallow aquifers contains pollutant arsenic. It may be that arsenic in the deep aquifer was mobilized during early diagenesis but has long since been flushed out by meteoric waters, which have been flushing the deep aquifer since well before the 18 Ka sea level minimum of around 130 m below the present level. In contrast, the Holocene shallow aquifer, largely less than 7 Ka in age, has not been so well flushed. Reduction of FeOOH will dissolve most of the surface-sorbed As(V) but not necessarily all the FeOOH, some of which may remain for later reduction. The As(V) will be reduced during FeOOH reduction (Zobrist *et al.* 2000) but not strongly re-sorbed, as As(III) sorbs less strongly to FeOOH than does As(V). A further reason why the deep aquifer is not arsenic polluted may be that sulfate reduction leads to sequestration of both iron and arsenic in diagenetic iron sulfides in the sediments, but not necessarily in the proportion in which they are seen in solution. At Lakshmipur, sulfate consumption (*i.e.* sulfate calculated from chlorinity minus measured sulfate), and so pyrite formation, is greater in the deep aquifer than in the shallow aquifer, so the deep aquifer has formed more pyrite and so sequestered more of its arsenic in diagenetic iron sulfides, which is not surprising given its much greater age.

An invocation of FeOOH reduction to explain arsenic pollution also needs to explain why there is seldom a good relation in groundwater between arsenic and iron, or between iron and bicarbonate. The co-variance between iron and bicarbonate (expected from Equation 2) may be poor because bicarbonate is produced by reduction of nitrate and sulfate, and weathering reactions (driven by methanogenic-CO₂), not by iron reduction alone. Poor correlations of arsenic with iron may arise because of resorption (partial, as arsenite sorbs less well than does arsenate) of arsenic onto fresh FeOOH exposed by dissolution, or because the As/FeOOH ratio may vary from place to place, for example in response to differing amounts of FeOOH on mineral surfaces and differing mineral abundances. Finally, poor correlations between iron and other constituents may result from the sampling protocol used, in both the regional survey of arsenic pollution in Bangladesh (Volume S2 of DPHE 1999) and the more detailed survey of groundwater chemistry in Nawabganj, Faridpur and Lakshmipur (S4 of DPHE 1999), which required that samples be filtered at the well head. Filtering reduces the amount of arsenic in well water (D. Chatterjee, *pers. comm.* 1999) presumably because, as previous work in Bangladesh had shown (BGS 1992), filtering iron-rich waters may remove iron from solution unless done under anoxic conditions in a glove bag, a technique not used in any survey in Bangladesh. More than 50% of dissolved iron may be lost at low (1-2 ppm) concentrations. At higher concentrations, losses may be proportionately smaller but they may still be significant in terms of mass. The iron oxyhydroxide precipitated on the filter may scavenge arsenic during filtration. Rural consumers do not filter well-water before use so the data for the regional survey may underestimate arsenic concentrations in waters and so the risk associated with water use. Estimates of the prevalence of arsenic-related health problems that are based on the DPHE data, such as Yu *et al.* (2000), should be viewed with this potential problem in mind.

5. THE REDOX DRIVER

The lateral and vertical differences in arsenic concentration in well water (Fig. 3; see also McArthur *et al.* 2001) do not arise simply from variations in the abundance of arsenic in aquifer sediments, since sediments in the Bengal Basin are not unusual in the amount of arsenic they contain. Concentrations of arsenic exceed the low tens of ppm only where traces of early-diagenetic, arsenical pyrite occur where organic matter is abundant (*e.g.* at 10 m beneath Samta village arsenic peaks at 60 mg kg⁻¹ where peat is found; Fig. 6). It is our postulate that pollutant arsenic in groundwater occurs where microbial reduction of FeOOH has released sorbed arsenic (and also reduced it) and organic matter is required to drive the process. We postulate that it is the distribution of organic matter in the aquifer sediments that is the main control on the distribution of arsenic pollution and this organic matter (OM) may take several forms.

Disseminated organic matter

Concentrations of < 0.5% total organic carbon (TOC) are typical of fluvial sands in the Bengal Basin (Ahmed *et al.* 1998; Nickson *et al.* 1998; AAN 1999; DPHE 1999) with a few higher values (*e.g.* 6% in Nickson *et al.* 1998, 2000) being found in organic-rich horizons that are discussed in a later section. Before being incorporated in the sediment, OM disseminated through the sands will have undergone some exposure to oxic degradation during riverine transport. Such exposure will have degraded the most reactive components of the OM, leaving it cellulose-rich and unfavourable for bacterial metabolisation. The amount, and probably the type, of OM combine to make it a source inadequate to drive redox to the extremes seen in the aquifer, which has water with up to 80 mg l⁻¹ of iron (Safiullah 1998) and up to 24 mg l⁻¹ of ammonium ion (DPHE 2000). A negligible contribution to FeOOH reduction, and to arsenic concentrations, is expected from this source.

Organic matter in silts and clays in overbank sediments

Overbank silts and (subordinate) clays contain more organic matter (0.3 to 1.5%) than do fluvial channel sands (Ullah 1998; Ravenscroft and Ahmed 1998) leading the latter authors to suggest that arsenic pollution might be present where buried overbank deposits occur and not where palaeo-active channels are found, because the former contain more organic matter than do the latter. Whether this is sufficient OM to drive the intense iron reduction, and severe arsenic pollution, in the Bengal basin is uncertain, but we hypothesise that it is unlikely. More importantly, the clays in overbank deposits are the least permeable strata in the sedimentary system and act as aquitards, so the availability of its OM for reaction is limited by the low permeability of such units. For this reason, and other reasons given below, we believe that such sediments are not the major redox driver for the severe arsenic pollution, although they will contribute background amounts of arsenic.

Peat Beds

Peat is common beneath the Old Meghna Estuarine Floodplain in Greater 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 (Fig. 6; Figs. 11 and p12 of 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). A further indicator of peaty sediment is the TOC content of some aquifer sediments; a sample 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. A further indicator of the degradation of much organic matter is the presence of ammonium in wells in concentrations ≤ 24 mg l⁻¹ (Hoque 1998; DPHE 2000) and the strong correlation between ammonium and phosphorus in well waters (McArthur *et al.* 2001). In addition, biogenic methane is common in groundwater over large areas (Ahmed *et al.* 1998; Hoque *et al.* 2001), in places in amounts sufficient to provide domestic fuel and to prevent suction-mode motorized pumping of groundwater; such methane can occur in the shallow aquifer only where substantial amount of organic matter are undergoing microbial degradation.

Through a combination of poverty and local pragmatism, many wells are completed with short screens at the top of the uppermost aquifer, in many cases but a short distance below a peat horizon. Were the wells deeper or the screens longer, the adverse impact on health would be avoided, or much reduced. If our arguments are correct, the areal distribution of arsenic pollution should correspond closely to the areal distribution of buried peat, so we explore this relation in Section 6 below. Whilst the indicators ammonium, phosphorus and methane show that biodegradation of peat is a major redox driver for arsenic pollution, a contribution to all of these pollutants occurs from degrading human organic waste in latrines, which are often sited within a few feet of wells. In areas where arsenic pollution is uncommon (Districts of Rajshahi and Natore) ammonium concentrations in wells correlates well with coliform counts (Fig. 9a). Where arsenic pollution is intense (Fig. 9b; Districts of Chandpur and Comilla) the correlation is poorer, and

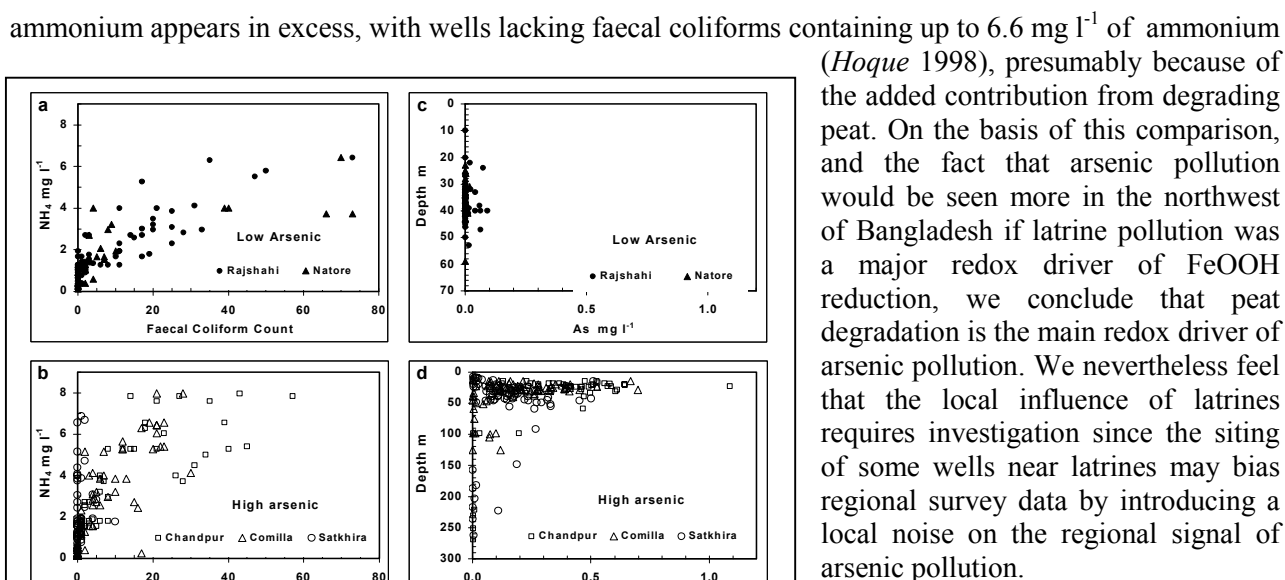


Fig. 9. Relation of ammonium and faecal coliform counts in Bangladesh groundwaters that are arsenic free (a) and arsenic polluted (b) and the relation of arsenic with depth in the same arsenic-free Districts (c) and arsenic-polluted Districts (d). Data from Hoque (1998) and DPHE (1999, 2000).

Kuehl (2000). Peat deposits are, and were, formed in waterlogged areas, rather than active river-channel deposits, a fact that helps to define today's areal pattern of pollution. Umitsu (1987, 1993) proposed that much peatland development occurred in the Bengal Basin during a climatic/sea-level optimum some 5 000 years BP. The high number of polluted wells with depths of between 20 and 60 metres may result from their being screened close to such peat horizons. The widespread occurrence of peat layers at shallow depth has been noted by Brammer (1996). If degradation of peat drives the redox processes that mobilize arsenic, then it should be possible to relate the distribution of arsenic to the transient palaeohydrological conditions, driven by Quaternary climatic changes, that controlled the formation of the paludal basins and related flood basins and mangrove swamps. Late Quaternary sea level changes were a major determiner of the distribution and hydrogeological properties of sediments in the Bengal Basin (BADC 1992; Umitsu 1993; Goodbred and Kuehl 1999, 2000; Ravenscroft 2001). When global sea level was 130 m lower than now at 18 Ka, the main rivers were deeply incised. The proto-Ganges and proto-Brahmaputra flowed within a series of stepped terraces between the Madhupur and Barind Tracts and Eastern Hills before flowing across a coastal plain some 50 - 70 m below present ground level. Incision of the major rivers probably followed their modern alignments, with the exception of the Lower Ganges which took a more direct route to the Swatch of No Ground (Umitsu 1993; Goodbred and Kuehl, 2000). The coastline then would have been far to the south of its present position. Monsoonal circulation was suppressed and rainfall reduced (Dawson, 1992). Consequently, the regional water table would have been

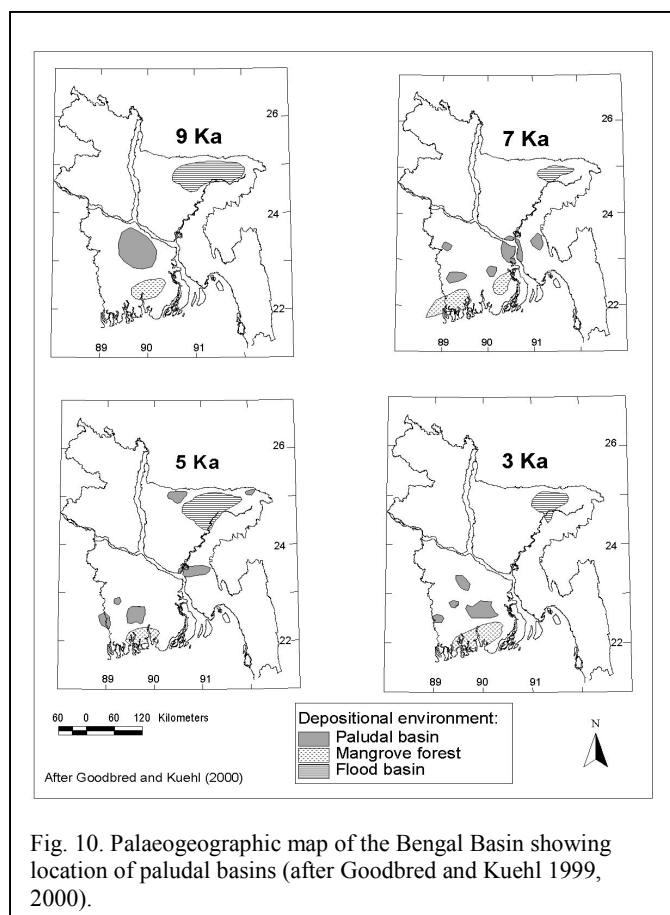


Fig. 10. Palaeogeographic map of the Bengal Basin showing location of paludal basins (after Goodbred and Kuehl 1999, 2000).

many tens of meters below ground. Hence in sediments that have survived the maximum Pleistocene incision, the consequent oxidation depleted organic matter and promoted recrystallization of iron phases. Aquifers formed from these sediments (Dupi Tila sands) are now oxic and so mostly free of arsenic pollution.

During the initial period of post-glacial sea level rise, alluvial aggradation was largely confined to the incised axial courses of the main rivers with most sediment being transferred to the submarine delta (Kudrass *et al.* 1999). At about 11 Ka, sea level intersected the coastal plain and wide estuaries extended deep into the major river valleys (BADC 1992; Hoque *et al.* 2000). Incomplete flushing of these sediments accounts for the occurrence of residual salinity (TDS \leq 12,000 ppm) in fine grained strata (BADC, 1992). Between 11 Ka and 7 Ka, onshore accumulation dominated as prograding deltas built out into a steadily rising sea level in the Bay of Bengal. Goodbred and Kuehl (1999) estimate that, during the mid-Holocene climatic optimum, the average discharge of the Ganges and Brahmaputra was 2.5 times as large as it is today. A flooded coastal platform, high discharge and elevated temperature created ideal conditions for the accumulation of extensive peat deposits. Since sea level rise was simultaneous with delta progradation, it is expected that the present depths of these paludal deposits increases inland.

Based on radiocarbon dating of OM from cored boreholes across southern Bangladesh, plus secondary sources, Goodbred *et al.* (2000) have mapped the approximate position of a series of paludal basins developed at 9, 7, 5 and 3 Ka during the Holocene transgression (Fig. 10). The maps shows few paludal basins in south-east Bangladesh, however, we believe that buried peat is more extensive here than implied by the map because, firstly many drillers report encountering peat in the region and, secondly, there are widespread discharges there of biogenic methane in shallow wells (BADC, 1992). Ahmed *et al.* (1998) showed that methane is spatially associated with Na–Cl groundwater, but is released at a shallower level in the aquifer system. This pattern is consistent with paludal basins building out into a retreating Holocene estuary. Further, peat and wood (mangrove?) samples have been encountered in deeper (70 – 130 m) drillings across the coastal plain and dated at between 30 and 40 Ka (J.W. Whitney, *pers. comm.* 1999) and so indicate the presence of a low-permeability, OM-rich, confining layer over the deep aquifer during the period of maximum incision at 18Ka.

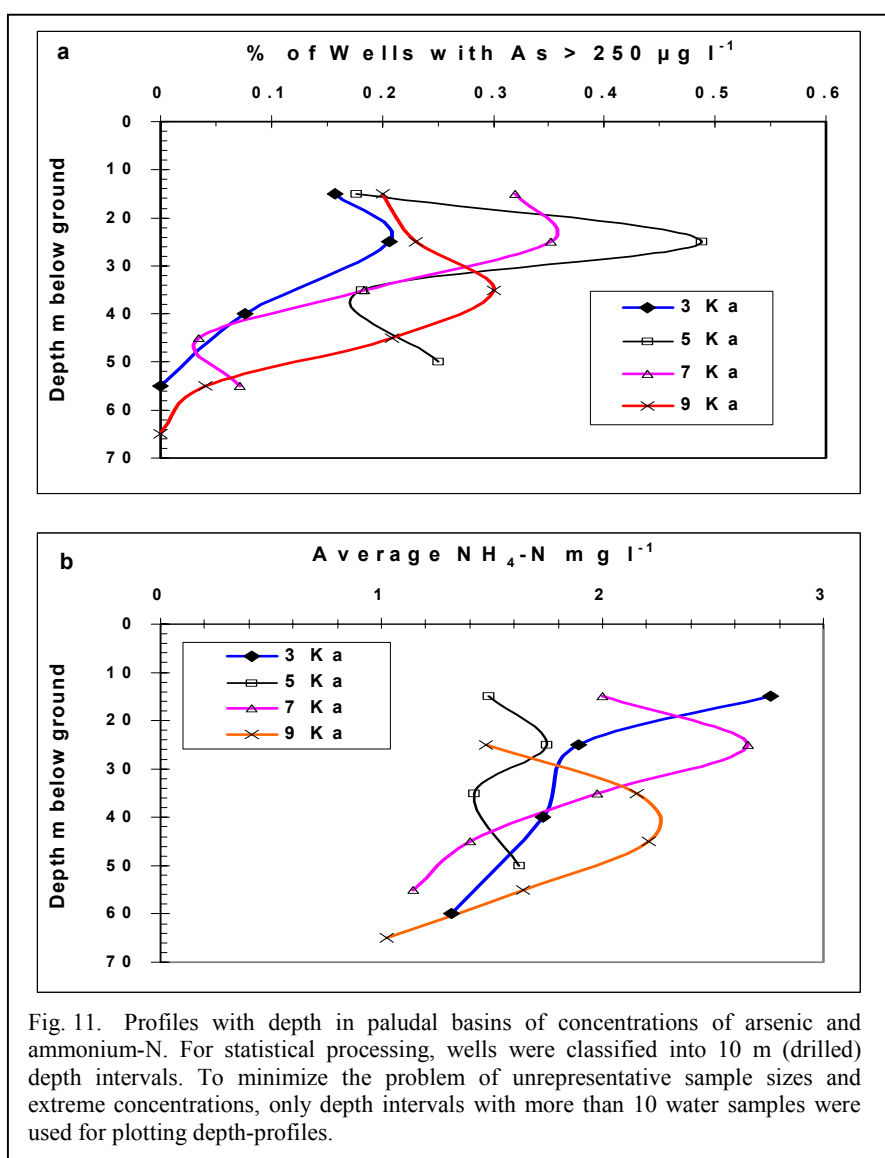
To test the idea that high arsenic concentrations are associated with paludal sedimentation, the locations of paludal basins from Goodbred *et al.* (2000) were superimposed upon the georeferenced arsenic analyses from DPHE (1999) and ammonium analyses from the same wells by Hoque (1998). Table 3 shows that the percentage of wells overlying the Holocene paludal basins polluted with arsenic is two to three times the national average.

Table 3. Arsenic contamination in areas of former paludal basins. Ages from Goodbred *et al.* (2000).

Age of Basin	No. of Wells	% of wells > 50 $\mu\text{g l}^{-1}$ As	% of wells >250 $\mu\text{g l}^{-1}$ As	Av. $\log_{10}(\text{As})$ $\mu\text{g l}^{-1}$
3Ka	77	45%	16%	0.033
5Ka	82	68%	34%	0.106
7Ka	160	62%	23%	0.060
9Ka	211	63%	18%	0.054

The proportion of polluted wells is least beneath the 3K basins. Beneath the older basins the proportions of polluted (>50 $\mu\text{g/l}$) wells are higher but similar to each other, however, the proportion of wells exceeding 250 $\mu\text{g/l}$ (or as mean concentration) is much more beneath the mid-Holocene (5Ka) basins, a distribution that may indicate multiple peat horizons in this rapidly subsiding basin. During the early Holocene, sea level rose more or less continuously until about 6 Ka and then stabilized whilst perhaps being a little higher during the climatic optimum at about 5 Ka. Therefore peat formed before 7 Ka should be more deeply buried, and if the peat-degradation hypothesis is correct this should be reflected in deeper peak of arsenic pollution.

Figure 11 shows the depth-profiles of arsenic represented as proportion of wells exceeding $250 \mu\text{g/l}$ in each 10 m depth-slice, and of the average ammonium concentration. Given the uncertainty of mapping the



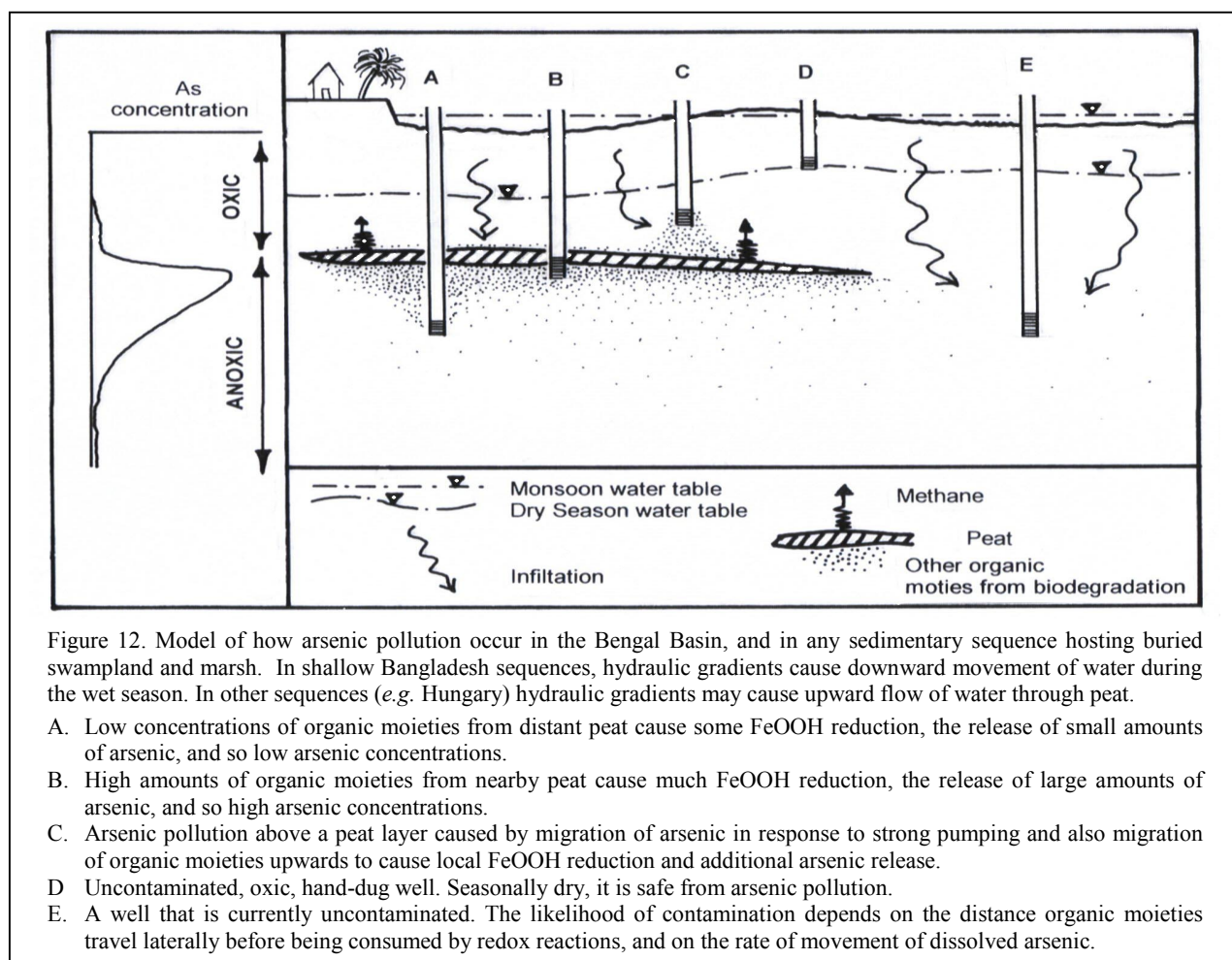
mobilization. In Sylhet, arsenic concentrations appear to peak at 60 m and also at 120 m, a distribution that may indicate major peat horizons at two distinct levels in this area of rapid subsidence.

6. PHYSICAL PROCESSES OF ARSENIC MIGRATION

Biodegradation of peat releases short-chain carboxylic acids and methylated amines that will drive FeOOH reduction and ammonium production (Bergman *et al.*, 1999). The fact that arsenic concentrations are so strongly dependent on depth (Fig. 3) suggests that these small organic molecules have not succeeded in migrating far, in a vertical sense, from their peat source. The extremely sharp upper limit at which arsenic pollution occurs (close to 10 m depth in most areas; Fig. 3) must define the maximum depth to which recharging water carries dissolved oxygen, which will prevent redox processes except oxic degradation. The asymmetry of the profiles may result from recharge passing through shallow peat layers and spreading through the aquifer sands the small organic molecules necessary to drive FeOOH reduction and arsenic release in the aquifer (where water is captured by wells with short screens placed at the top of the aquifer). This degree of asymmetry in depth-distribution, and the depth of penetration by OM and so arsenic, will be governed by the vertical permeability distribution and by the depth of wells in a region. A difficulty with this postulate is that modern peats are typically underlain by impermeable clays (Brammer, *pers. comm.*

locations of former paludal basins, only general trends should be expected, particularly since some of the basins locations overlap and would produce complex profiles. Furthermore, the ammonium that may be derived from decomposition of peat must be judged against a background of widespread faecal contamination. Nevertheless there are clear signatures of the 3 Ka and 9 Ka basins in both the arsenic and the ammonium profiles. The 3 Ka profiles peak at a shallow level and decline rapidly with depth. The 9 Ka profiles have distinct peak that is clearly deeper than in the other profiles. The 5 Ka and 7 Ka profiles are similar to each other, which is not surprising since sea-level rise levelled off at about 6 Ka. The coincidence of peak ammonium and arsenic concentrations both with each other and with the increasing age of paludal deposit is therefore consistent with our proposal that decomposition of peat is the critical redox driver leading to arsenic

2001) and so older peats may also be so underlain, thereby restricting downward migration of organic moieties; later channels may cut through peat deposits as rivers alter course and so provide pathways through channel sands for dissolved organic material to move downwards (Brammer, *pers. comm* 2001). A schematic of the process of how arsenic pollution affects individual wells is shown in Fig. 12.



If degradation of peat drives the reduction process, dissolved organic matter has migrated into aquifer sands that are adjacent to the peat horizons and there caused arsenic pollution of water wells. But pollution is very patchy within an area because migration has not spread arsenic or organic reaction products throughout the aquifer. The shallow groundwater flow system in Bangladesh is extremely complex (van Wonderen, 2001). Secondary migration (through local and regional circulation) is driven by the interaction of low regional hydraulic gradients, micro-topographic effects, surface water bodies, deep-rooted vegetation, seasonal flooding and waterlogging. Human intervention (pumping and land use) further complicates these processes by inducing seasonally alternating vertical and horizontal components of flow that are superimposed on topographic gradients that operate on different and sometimes opposing directions. These processes result in a small aquifer throughflow measured on a scale of kilometers, but a rapid turnover of water in the upper 5 to 10 m (including the 3 to 5 m zone of water table fluctuation). Furthermore, small scale circulation of water and solutes in the underlying zone - a few meters to a few tens of meters thick - will be significant thereby providing a mechanism for redistributing small organic molecules and arsenic from low - to high-permeability zones.

DPHE (1999) modelled the effects of (modern) natural fluctuations and flow (*i.e.* no pumping) on the movement of arsenic away from low-permeability (0.01 - 0.1 m/d) 'hot-spots' within fine sand (10 m/d) under conditions based on experience at Faridpur. Simulations were run for a 500 year period and included advection and dispersion with and without the effects of sorption. Without sorption, lateral spreads of up to 200 - 300 m and vertical spreads of 10 - 50 m were predicted. Including sorption reduces the predicted lateral and vertical spreads to around 25 m and < 10 m respectively. Thus it seems feasible for organic

matter and so arsenic released in shallow, low permeability beds to have polluted the underlying aquifers to a depth of 10 to 20 m over a geologically reasonable period of 3000 to 9000 years, but not to a greater depth. The introduction of pumping creates stronger vertical components of flow, and induces leakage of both organic matter and arsenic into the underlying aquifers. When wells are screened close to peat beds, the result is inevitably to accelerate these processes and a breakthrough phenomenon is to be anticipated (Cuthbert 1999).

7. IMPLICATIONS

Arsenic pollution by oxidation of arsenical pyrite is a mechanism that is valid for oxic environments, typically surface waters. It may apply to the subsurface where high-permeability allows polluted surface water access to the subsurface, as in Zimapán, Mexico (*Armienda et al.* 1997). It may apply where oxic conditions invade a previously anoxic environment, for example, one hosting sulfide ore such as occurs in northeastern Wisconsin (*Schreiber et al.* 2000), where a commercially prospective sulfide ore-body, up to 3 metres thick, (*A. Weissbach, pers. comm.* 2000) is exposed to oxic conditions in domestic boreholes. Oxidation of the ore results in pollution of groundwater by high concentrations of arsenic ($\leq 15\,000\ \mu\text{g l}^{-1}$), sulfate ($< 618\ \text{mg l}^{-1}$), iron ($< 160\ \text{mg l}^{-1}$) and acidity ($\text{pH} \geq 2.1$) (*Schreiber et al.* 2000; *A. Weissbach pers. comm.* 2000). Despite the presence of this massive sulfide ore, wells cased through the ore zone, and drawing water from a few metres below it, contain less than $50\ \mu\text{g l}^{-1}$ of arsenic confirming that it is access of oxygen to boreholes that causes pyrite oxidation and arsenic pollution (*A. Weissbach, pers. comm.* 2000).

Where arsenic pollution occurs in most subsurface, and most anoxic, environments, the pyrite oxidation model is inappropriate and a different model is needed. Reduction of FeOOH (invoked before for groundwater *e.g.* *Gulens et al.* 1979; *Matisoff et al.* 1982; *Cullen and Reimer* 1989; *Korte* 1991; *Bhattacharya et al.* 1997; *Nickson et al.* 1998, 2000; *McArthur et al.* 2001; refs. therein) will serve in most instances. As the process is generic and not site specific it should be tested for wherever naturally-occurring arsenic pollution occurs in groundwater in alluvial aquifers, such as in Argentina [*Nicolli et al.* 1989; *Garcia et al.* 2000], Taiwan [*Chen et al.* 1994], China [*Wang and Huang* 1994; *Sun et al.* 2000], Hungary, and the USA [*Welch et al.* 2000]. In this context, it is noteworthy that the arsenic pollution of deep wells in Hungary is accompanied by high concentrations of ammonium, iron and methane (*M. Csanady, pers. comm.* 2000), presumably derived from deeply buried peat deposits that drive iron reduction and arsenic pollution. Severe arsenic pollution has now been reported by *Berg et al.* (2001) in groundwater wells supplying the city of Hanoi, in the Red River Basin of Vietnam, wells analysed in a recent survey of pollution (*BGS* 1996) that did not include analyses for arsenic, a WHO-listed parameter for drinking water. The area around Hanoi hosts abundant peat deposits (*BGS* 1996) and there are striking similarities in the composition of ground water in arsenic-affected areas of Bangladesh and in the vicinity of Hanoi; both areas have high concentrations of bicarbonate, iron, phosphorus and ammonium. Arsenic pollution in Taiwan occurs in an environment that is interpretable as swampy and organic-rich, from the statement of *Tseng et al.* (1968, p460) that “Waters tapped from organic black sediments of the lagoons in the endemic area are full of soluble salts such as arsenic and methane gas”.

It is likely that any fluvial or deltaic basin that has hosted marshland and swamp will be prone to severe arsenic pollution of borehole water. The specific Holocene environmental history of the Bengal basin accounts for the particular geometry of arsenic contaminated aquifers in Bangladesh. However, a set of globally applicable parameters – the depth of pre-Holocene incision, the relative rates of sea level rise and alluvial aggradation, and the Holocene temperature and rainfall records – provide a general model for predicting the possible occurrence of arsenic in any basin. While concentrations of arsenic of, say, 2 to $30\ \mu\text{g/l}$ may prove quite common in recent alluvial aquifers in humid tropical environments, frequent high concentrations ($> 200\ \mu\text{g l}^{-1}$) may require the special condition of extreme accumulation of organic matter. This condition may involve a flooded Holocene marine (or possibly lacustrine) platform to provide the accommodation space for paludal deposits, that in turn create the redox driver to mobilize large amounts of arsenic. In many areas of the world, agriculture and urbanization occur on lowland coastal plains in a setting similar in type, although not always in scale, to that in Bangladesh. Such areas might be expected to suffer from arsenic pollution, and it should be looked for. Vulnerable regions include the deltas of tropical rivers, such as the Mekong, Red, Irrawaddy, and Chao Phraya rivers, and the northern coastal plains of Java and Sumatra.

8. CONCLUSIONS

Neither pyrite oxidation, nor competitive exchange of fertilizer-phosphate for sorbed arsenic, cause arsenic pollution of groundwater in the Bengal Basin. Indeed, pyrite in Bangladesh aquifers is a sink for, not a source of, arsenic. Pollution by arsenic occurs because FeOOH is microbially reduced and releases its sorbed load of arsenic to groundwater. The reduction is driven mostly by the microbial metabolism of buried peat deposits. The subordinate role of human organic waste in latrines as a redox driver for arsenic pollution requires investigation. Dissolved phosphorus comes from FeOOH, as it is reductively dissolved, and from the degradation of buried peat deposits and subordinately, organic human waste in latrines. Dissolved ammonium in the aquifer derives mostly from the microbial fermentation of buried peat deposits and, subordinately, from degradation of organic human waste in latrines. Ammonium ion is not, therefore, a reliable indicator of faecal contamination. Reduction of FeOOH, and release of sorbed arsenic, serves as a generic model for arsenic pollution of aquifers where waters are anoxic because organic matter is abundant, e.g. in deltaic or fluvial areas that hosted peat basins during climatic optimums and/or periods of rapidly rising sea level.

Acknowledgements. PR thanks the Department of Public Health Engineering, Government of Bangladesh, for permission to use data from its project 'Groundwater Studies for Arsenic Contamination' and also Steven Goodbred Jr., State University of New York, for access to pre-publication maps of paludal basins, and John Whitney of the US Geological Survey for access to radiocarbon dates. JMMcA thanks the Friends of UCL for travel funds to visit Bangladesh and West Bengal before the preparation of this paper, and the British Council for travel funds to visit West Bengal in 2000. We thank Spiros Pergantis and Maria Miguens-Rodriguez for analysis for MMAA and DMAA in Bangladesh water samples, S. Safiullah, S.M. Tareq and M.M. Rahman for collecting water samples from Faridpur, and Richard Loeppert, Hugh Brammer, and an anonymous reviewer for constructive comments that improved the script.

References

- AAN (1999). Arsenic contamination of groundwater in Bangladesh. Interim report of the research at Samta village. Report of the Asian Arsenic Network, April, 1999, 90pp.
- AAN (2000). Arsenic contamination in groundwater and hydrogeological background in Samta village, western Bangladesh. Report of the Asian Arsenic Network, July, 2000, 31pp.
- Acharyya S.K., Lahiri S., Raymahashay B.C. and Bhowmik A. (2000). Arsenic toxicity of groundwater in parts of the Bengal Basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environmental Geology*, 39, 1127-1137.
- Aggett J. and O'Brien, G.A. (1985) Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. *Environ. Sci. Technol.*, 19, 231-238, 1985.
- Ahmann D., Krumholz L.R., Hemond H.H., Lovley D.R. and Morel F.M.M. (1997). Microbial mobilization of arsenic from sediments of the Aberjona watershed. *Environ. Sci. Technol.*, 31, 2923 - 2930.
- Ahmed K.M., Hoque M., Hasan M.K. Ravenscroft P. and Chowdhury L.R. (1998). Occurrence and origin of water well methane gas in Bangladesh. *Jour. Geol. Soc. India*, 51, 697-708.
- Armienta M.A., Rodriguez R., Aguayo A., Cenicerros N., Villaseñor G. and Cruz O. (1997). Arsenic contamination of groundwater at Zimapán, Mexico. *Hydrogeology Journal*, 5, 39-46.
- BADC (1982). ADB Second Tubewell Project Feasibility Study, Vol 3: Groundwater. Sir M. MacDonald & Partners and Hunting Technical Services. Report for Bangladesh Agricultural Development Corporation and Asian Development Bank.
- BADC (1992). Deep Tubewell II Project. Final Report. Mott MacDonald Ltd. and Hunting Technical Services. Report for Bangladesh Agricultural Development Corporation and Overseas Development Administration (UK).
- Banfield J.F., Nealson K.H. and Lovley D.R. (1998). Geomicrobiology: Interactions between microbes and minerals. *Science*, 280, 5360, 54-55.
- Bhattacharya P., Chatterjee D. and Jacks G. (1997). Occurrence of arsenic-contaminated groundwater in alluvial aquifers from the Delta Plain, Eastern India: options for a safe drinking water supply. *Water Res. Dev.*, 13, 79-92.
- Belzile N. and Tessier A. (1990). Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. *Geochim. et Cosmochim. Acta*, 54, 103-109.
- Berg, M, Tran H.C., Nguyen T.C., Pham H.V., Schertenleib R. and Giger W. 2001. Arsenic contamination of ground and drinking water in Vietnam: a human health threat. *Environ. Sci. Technol.*, 35, 2621-2626.

- Bergman I., Lundberg P. and Nilsson M. (1999). Microbial carbon mineralisation in an acid surface peat: effects of environmental factors in laboratory incubations. *Soil Biol. Biochem.*, 31, 1867-1877.
- BGS (1992). Technical Report WD/92/43R. "Hydrochemical character of the main aquifer units of central and northeastern Bangladesh and possible toxicity of groundwater to fish and humans", and Supplement WD/92/44R, 1992.
- BGS (1996). Technical Report WC/96/22. The effect of urbanization on the groundwater quality beneath the city of Hanoi, Vietnam. British Geological Survey.
- Borho M. and Wilderer P. (1997). A reliable method for preservation and determination of arsenate(III) concentrations in groundwater and water works samples. *J. Water SRT - aqua*, 46, 138-143.
- Brammer H. (1996) The Geography of the Soils of Bangladesh. University Press Ltd, Dhaka.
- Chakraborti D. (2001). Probable explanation why dugwells are safe with respect to arsenic in the arsenic affected villages of West Bengal-India and Bangladesh. <http://www.geocities.com/broadway/wing/3014/dcsoesju.html>
- Chapelle F.H. (2000). The significance of microbial processes in hydrogeology and geochemistry. *Hydrogeol. Journal*, 8, 41-46.
- Chen, S-L., Dzung, S.R. Yang, M-H., Chiu, K-H. Shieh, G-M. and Wai, C.M., Arsenic species in groundwaters of the Blackfoot disease area, Taiwan. *Environ. Sci. Technol.*, 28, 877-881, 1994.
- Cherry J.A., Shaikh A.U. Tallman D.E. and Nicholson R.V. (1979). Arsenic species as an indicator of redox conditions in groundwater. *Journal of Hydrology*, 43, 373-392.
- Cullen W.R. and Reimer K.J. (1989). Arsenic speciation in the environment. *Chem. Rev.*, 89, 713-764.
- Cuthbert, M. (1999). Modelling the transport of arsenic to hand tubewells in the Holocene alluvial aquifer of Bangladesh. MSc Thesis (Unpub.), University College London.
- Dawson, A.G. (1992). Ice Age Earth. Routledge, London.
- Dhar R.K., Biswas B.K., Samanta G., Mandal B.K., Chakraborti D., Roy S., Jafar A., Islam A., Ara G., Kabir S., Khan A.W., Ahmed S.K. and Hadi S.A. (1997). Groundwater arsenic calamity in Bangladesh. *Current Science*, 73, 48-59.
- Dowdle P.R., Laverman A.M. Oremland R.S. (1996). Bacterial dissimilatory reduction of arsenic(V) to arsenic (III) in anoxic sediments. *Applied and Environmental Microbiology*, 62, 1664-1669.
- DPHE (1999). Groundwater Studies for Arsenic Contamination in Bangladesh. Final Report, Rapid Investigation Phase. Department of Public Health Engineering, Government of Bangladesh. Mott MacDonald and British Geological Survey.
- DPHE (2000). Groundwater Studies for Arsenic Contamination in Bangladesh. Supplemental data to Final Report, Rapid Investigation Phase. <http://www.bgs.ac.uk/arsenic/Bangladesh/home.htm>. Department of Public Health Engineering, Government of Bangladesh. British Geological Survey.
- Frisbie S.H., Maynard D.M. and Hoque B.A. (1999). The nature and extent of arsenic-affected drinking water in Bangladesh. In: Metals and Genetics (B. Sarkar, ed.), Kluwer Academic / Plenum Press, New York, 1999.
- Guha Mazumder, D.N., Chakraborty, A.K., Ghose, A., Gupta, J.D., Chakraborty, D.P., Dey, S.B., Chattopadhyay, N., 1988: Chronic arsenic toxicity from drinking tubewell water in rural West Bengal. *Bulletin of the World Health Organization*, 66(4), pp. 499-506.
- Garcia M.G., Fernández D.S., del Valle Hildago M. and Blesa M.A. (2000). Arsenic in groundwaters of the southeast of Tucumán Province, Argentina. In: *Groundwater: Past Achievements and Future Challenges* Silsoe et al. (eds), Balkema, Rotterdam, p503-508.
- Gavrieli I., Zheng Y., van Geen A., Stute M., Dhar R., Ahmed K.M., Simpson J. and Goldstein S.L. (2000). Hydrogeochemical study of arsenic contamination in Bangladesh groundwater - the role of redox condition. *Journal of Conference Abstracts*, 5, 435, 2000.
- Goodbred S.L., Jr. and Kuehl S.A. (1999). Holocene and modern sediment budgets for the Ganges-Brahmaputra river system: Evidence for highstand dispersal to flood-plain, shelf and deep-sea depocenters. *Geology*, 27, 559-562.
- Goodbred S.L., Jr. and Kuehl S.A. (2000). The significance of large sediment supply, active tectonism, and eustasy on margin sequence development: Late Quaternary stratigraphy and evolution of the Ganges-Brahmaputra delta. *Sedimentary Geology*, 133, 227-248.
- Gulens J., Champ D.R. and Jackson R.E. (1979). Influence of redox environments on the mobility of arsenic in groundwater. In: Chemical modeling in aqueous systems; speciation, sorption, solubility, and kinetics, E.A. Jenne (Ed.), American Chemical Society Symposium Series, 93, 81-95
- Hall G.E.M., Pelchat J.C., Gauthier G. (1999). Stability of inorganic arsenic(III) and arsenic(V) in water samples. *Journal of Analytical Atomic Spectrometry*, 14, 2, 205-213.
- Hoque B.A. (1998). Biological contamination of tubewell water. Environmental Health Programme; International Centre for Diarrhoeal Disease Research, Bangladesh.
- Hoque M., Hasan M.K. and Ravenscroft P. (2001). Investigation of Groundwater Salinity and Gas Problems in Southeast Bangladesh. In: A.A. Rahman, and P. Ravenscroft (eds.). *Groundwater Resources and Development in Bangladesh*. Bangladesh Centre for Advanced Studies, University Press, Dhaka.
- Ishiga H. Dozen K., Yamazaki C., Ahmed F., Islam B. Raham H. Sattar A Yamamoto H and Itoh K. (2000). Geological constraints on arsenic contamination of groundwater in Bangladesh. 5th Forum on Arsenic Contamination, Yokohama, Japan, 2000.

- Islam M.S. and Tooley M.J. 1999. Coastal and sea level changes during the Holocene in Bangladesh. *Quaternary International* 55, 61-75.
- JICA (1976). Feasibility study report for Jamuna River bridge construction project. Volume VI : geology and stone material. Japan International Co-operation Agency.
- Karim M. Komori Y. and Alam M. (1997). Arsenic occurrence and depth of contamination in Bangladesh. *Jour. Environ. Chem.*, 7, 783-792.
- Korte N. (1991). Naturally-occurring arsenic in groundwaters of the midwestern United States. *Environmental Geol. Water Sci.*, 18, 137-141.
- Korte, N.E. and Fernando, Q. (1991). A review of arsenic(III) in groundwater. *Crit. Rev. In Environm. Control*, 21, 1-39.
- Kudrass H.R., Spiess V., Michels M., Kottke B. and Khan S.R. (1999). Transport processes, accumulation rates and a sediment budget for the submarine delta of the Ganges – Brahmaputra and the Swatch of No Ground, Bangladesh. International Seminar *Quaternary Development and Coastal Hydrodynamics of the Ganges Delta in Bangladesh. Geological Survey of Bangladesh*. Dhaka, 20-21 September, 1999.
- Lovley D.R. (1997). Microbial Fe(III) reduction in subsurface environments. *FEMS Microbiology Reviews*, 30, 305-313.
- Lovley D.R. and Anderson R.T. (2000). Influence of dissimilatory metal reduction on the fate of organic and metal contaminants in the subsurface. *Hydrogeol. Journal*, 8, 77-88.
- Mallick S. and Rajagopal N.R. (1996). Groundwater development in the arsenic-affected alluvial belt of West Bengal – Some Questions. *Current Science*, 70, 956-958.
- Mandal B.K., T.R. Chowdhury G., Samanta G., Mukherjee D., Chanda C.R., Saha K.C. and Chakraborti D. (1998). Impact of safe water for drinking on five families for 2 years in West Bengal, India. *Sci. Total Environ.*, 218, 185-201.
- Manning B.A. and Goldberg S. (1997). Adsorption and stability of arsenic(III) at the clay mineral-water interface. *Environ. Sci. Technol.*, 31, 20005-2011.
- Matisoff G., Khourey C.J., Hall J.F., Varnes A.W. and Strain W. (1982). The nature and source of arsenic in Northeastern Ohio ground water. *Ground Water*, 20, 446-455.
- McArthur J.M., Ravenscroft P., Safiullah S. and Thirlwall M.F. (2001). Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Res. Research*, 37, 109-117.
- Mok, W.M. and Wai, C.M., Mobilization of arsenic in contaminated river sediment. In: *Arsenic in the Environment; Part 1: Cycling and Characterization*, J. Nriagu (ed.), J. Wiley and Sons, 1994, 99-118.
- Monsur H. (1995). An Introduction to the Quaternary Geology of Bangladesh. International Geological Correlation Programme IGCP-347. Rehana Akhter, Dhaka.
- Morgan J.P. and McIntire W.G. (1959) Quaternary geology of the Bengal Basin, East Pakistan and India. *Geol. Soc. Amer. Bull.*, 70, 319-342.
- Nealson K.H. (1997). Sediment bacteria: Who's there, what are they doing, and what's new? *Annual Reviews in Earth Planet. Sci.*, 25, 403-434.
- Nickson R.T., McArthur J.M., Burgess W.G., Ravenscroft P., Ahmed K.M. and M. Rahman (1998). Arsenic Poisoning of Bangladesh Groundwater. *Nature*, 395, 338.
- Nickson R.T., McArthur J.M., Ravenscroft P., Burgess W.G. and Ahmed K.M. (2000). Mechanism of arsenic poisoning of groundwater in Bangladesh and West Bengal. *Appl. Geochem.*, 15, 403-413.
- Nicolli H.B., Suriano J.M., Gomez Peral M.A., Ferpozzi L.H. and Baleani O.A. (1989). Groundwater contamination with arsenic and other trace elements in an area of the Pampa, Province of Córdoba, Argentina. *Environ. Geol. Water Sci.*, 14, 3-16.
- NMIDP (1997). National Minor Irrigation Census 1995/96. National Minor Irrigation Development Project. Ministry of Agriculture, Dhaka. Halcrow/DHV Consultants.
- PHED (1991). Final Report, National Drinking Water Mission; Submission Project on Arsenic Pollution in Groundwater in West Bengal. Steering Committee, Arsenic Investigation Project, Public Health Engineering Department, Govnt. West Bengal.
- Ravenscroft, P. and Ahmed, K. M. (1998). Regional Hydrogeological Controls on the Occurrence of Arsenic in Groundwater in the Bengal Basin. In: International Conference on Arsenic Contamination in Groundwater: Cause, Effect and Remedy. Calcutta and Dhaka 7-11 February, 1998.
- Ravenscroft P. (2001). An Overview of the Hydrogeology of Bangladesh. In: A.A. Rahman, and P. Ravenscroft (eds.). *Groundwater Resources and Development in Bangladesh*. Bangladesh Centre for Advanced Studies, University Press, Dhaka.
- Ravenscroft P. and McArthur J.M. (in review). Boron pollution, sodium excess, from exchange processes in groundwater in Bangladesh. *Water Resources Research*.
- Reimann K-U. (1993). Peat deposits of Bangladesh. The Geology of Bangladesh, K-U Reiman, Gebruder Borntraeger, Berlin, 1993.
- Roy Chowdhury T. *et al.* (1999). Comment on Nickson *et al.* 1998, Arsenic poisoning of Bangladesh groundwater, *Nature*, 401, 545-546.

- Safiullah S. (1998). CIDA Arsenic Project Report: Monitoring and mitigation of arsenic in the ground water of Faridpur Municipality. Jahangirnagar University, Dhaka, Bangladesh, 96pp.
- Savage, K.S., Tracey, N.T., O'Day, P.A., Waychunas, G.A. and Bird, D.K., Arsenic speciation in pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County, California. *App. Geochem.*, 15, 1219-1244, 2000.
- Schreiber M.E., Simo J.A. and Freiberg P.G. (2000). Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. *Hydrogeol. Jour.*, 8, 161-176.
- Singh I.B., Srivastava P., Sharma S., Sharma M., Singh D.S., Rajagopalan G. and Shukla U.K. (1999). Upland interfluvial (doab) deposition: alternative mode to muddy overbank deposits. *Facies*, 40, 197-210. Erlangen, Germany.
- Smith A.H., Lingas E.O., and Rahman M. (2000). Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bulletin World Health Org.* 78 (9), 1093-1103.
- Stolz J.F. and Oremland R.S. (1999). Bacterial respiration of arsenic and selenium. *FEMS Microbiology Reviews*, 23, 615-627.
- Sun, G.F., Pi, J.B., Li, B., Guo, X.Y., Yamavchi, H. and Yoshida, T., Introduction of present arsenic research in China. In: Abstract, 4th Int. Conf. Arsenic Exposure and Health Effects, San Diego, June, 2000, p9.
- Tseng W.P., Chu H.M., How S.W. Fong J.M., Lin C.S. and Shu Yeh (1968). Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan. *Jour. National Cancer Institute*, 40, 453-463.
- Ullah S.S. (1998). Geochemical mapping and speciation of arsenic in groundwater of Faridpur municipality, Bangladesh. *Journal Bangladesh Academy of Sciences*, 22, 143-147.
- Umitsu M. (1987). Late Quaternary environment and landform evolution in Bengal. *Geog. Rev. Japan, Ser. B*, 60, 164-178.
- Umitsu M. (1993). Late Quaternary environment and landforms in the Ganges Delta. *Sedimentary Geology*, 83, 177-186.
- van Wonderen, J. (2001). The use of groundwater models. In: A.A. Rahman, and P. Ravenscroft (eds.). Groundwater Resources and Development in Bangladesh. Bangladesh Centre for Advanced Studies, University Press, Dhaka.
- Volke P. and Merkel B. (1999). Using of a new field analysis method to investigate the stability of arsenic and its inorganic species in aquatic systems *Acta Hydrochim. Hydrobiol.*, 1999, 27, 230-238.
- Wang, L. and Huang, J., Chronic arsenicism from drinking water in some areas of Xinjiang, China. In: Nriagu J.O. (ed) Arsenic in the Environment. Part II: Human Health and Ecosystem Effects. Wiley, New York, 159-172, 1994.
- Wangkarn S. and Pergantis S.A. (2000). High-speed separation of arsenic compounds using narrow-bore high-performance liquid chromatography on-line with inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.*, 15, 627-633.
- Welch, A.H., Westjohn, D.B., Helsel, D.R. and Wanty, R.B., Arsenic in ground water of the United States: occurrence and geochemistry. *Ground Water*, 38, 589-604, 2000.
- Whitney J.W., Pavich M.J., Huq M.A. Khorshed A.K.M. (1999). The age and isolation of the Madhupur and Barind Tracts, Ganges – Brahmaputra Delta, Bangladesh. International Seminar *Quaternary Development and Coastal Hydrodynamics of the Ganges Delta in Bangladesh*. Geological Survey of Bangladesh. Dhaka, 20-21 September, 1999.
- Yu W.H., Harvey C.M. and Harvey C.F. (2000). Estimating the health effects of arsenic contaminated groundwater in Bangladesh : a combined geostatistical and epidemiological model. Abstract, AGU Fall meeting, San Francisco, December, 2000.
- Zobrist J., Dowdle P.R. Davis J.A. and Oremland R.S. (2000). Mobilization of arsenite by dissimilatory reduction of adsorbed arsenate. *Environmental Science and Technology*, 34, 4747-4753.