12 Sorption and transport

12.1 Evolution of the groundwater arsenic problem in the Bengal Basin

In this chapter we discuss the possible mechanisms by which the Bangladesh groundwater arsenic problem may have arisen. Central to this are the concepts of sorption and transport. There are many uncertainties and much of what is discussed below is speculation that needs to be tested. We begin by reviewing some of the more firmly established conclusions from our work and that of others.

12.1.1 Established background information

While it is too early to be able to say unequivocally how the high arsenic concentrations in groundwater in the Bengal Basin have evolved, enough is known to be able to speculate on the likely processes. The following observations are now reasonably well supported by data and can form a basis for such speculation.

- Arsenic is not that rare in the natural environment. It is found in all sediments, typically at total concentrations from a few mg kg^{-1} up to about 10–15 mg kg^{-1}. Bangladesh sediments do not appear to be exceptional in this respect. Furthermore, groundwaters with high As concentrations are now being found under broadly similar conditions to those of the Bengal Basin in many places in the world.
- Arsenic, especially As(V), is strongly sorbed by Fe(III) oxides – this is known from laboratory studies with pure oxides and can also be inferred from the analysis of iron oxides from Bangladesh sediments. There is often a good correlation between the iron and arsenic concentrations in the sediments, both in terms of 'total' concentrations and 'oxalate-extractable' concentrations. Limited sediment data suggest that areas of arsenic-contaminated groundwaters in Bangladesh tend to be found in areas with sediments containing relatively high concentrations of extractable Fe (and associated As).
- As(V) sorption by iron oxides is quite similar to that of phosphate and in the absence of other specifically adsorbed ions is characterised by a highly nonlinear sorption isotherm. This means that even at very low arsenic concentrations in solution, the loading of arsenic on the surface can be relatively high. This feature is responsible for maintaining the very low concentration of As usually found in natural waters. As a consequence of this, even a small disturbance to this equilibrium can release relatively large quantities of As to the surrounding water.
- High arsenic concentrations in groundwaters from the Bengal Basin are always associated with strongly reducing conditions and there is some evidence that the more reducing, the greater the concentration but the relationship is far from perfect and is of itself not good enough for predicting groundwater arsenic concentrations. The groundwaters also have relatively high concentrations of bicarbonate and of other redox-sensitive species such as iron, manganese, ammonium and nitrite. They also contain relatively low concentrations of sulphate and nitrate.
- High-arsenic groundwaters are often associated with high-iron groundwaters but the correlation is far from perfect and is not sufficiently good to be generally useful for predicting groundwater arsenic concentrations. Correlations with other water quality parameters such as bicarbonate, sulphate and phosphate may be locally significant but tend to be weaker than with iron.
- While some groundwaters do contain relatively high concentrations of sulphate, particularly in northern Bangladesh, these do not correlate with the high-As groundwaters. If sulphide oxidation were the main mechanism for As release, sulphate and arsenic concentrations would also be expected to be greatest in the more oxidised zone close to the soil surface. The results from our piezometers do not demonstrate this – arsenic concentrations tend to be somewhat smaller in the shallowest groundwaters. Therefore sulphide mineral oxidation is unlikely to be the source of the As in the high-As groundwaters.
- The low concentrations of sulphate, typically < 5 mg L^{-1} sulphate, tend to be associated with the strongly-reducing high-As groundwaters. There is evidence for the precipitation of iron sulphides in some sediments. Framboidal, authigenic pyrite is occasionally observed. This would account for the disappearance of residual seawater sulphate. Some As would have been scavenged from the pore water during the formation of these sulphide minerals.
- The range of As concentrations in Bangladesh groundwaters is large (more than four orders of magnitude). There is a good deal of short-range variation, for example within a village, but there are also very distinct regional patterns. The same can probably also be said about the sediments: much local variation but regional differences too.
- The depth of the well is very important which in turn may reflect the importance of the age of the sediment. Groundwater from deep wells usually has a low As concentration even in areas where the shallow wells are heavily contaminated. While the original deep well data was for only a relatively small region of Bangladesh, recent drilling in other areas (and in West Bengal) seems to confirm this observation more broadly.

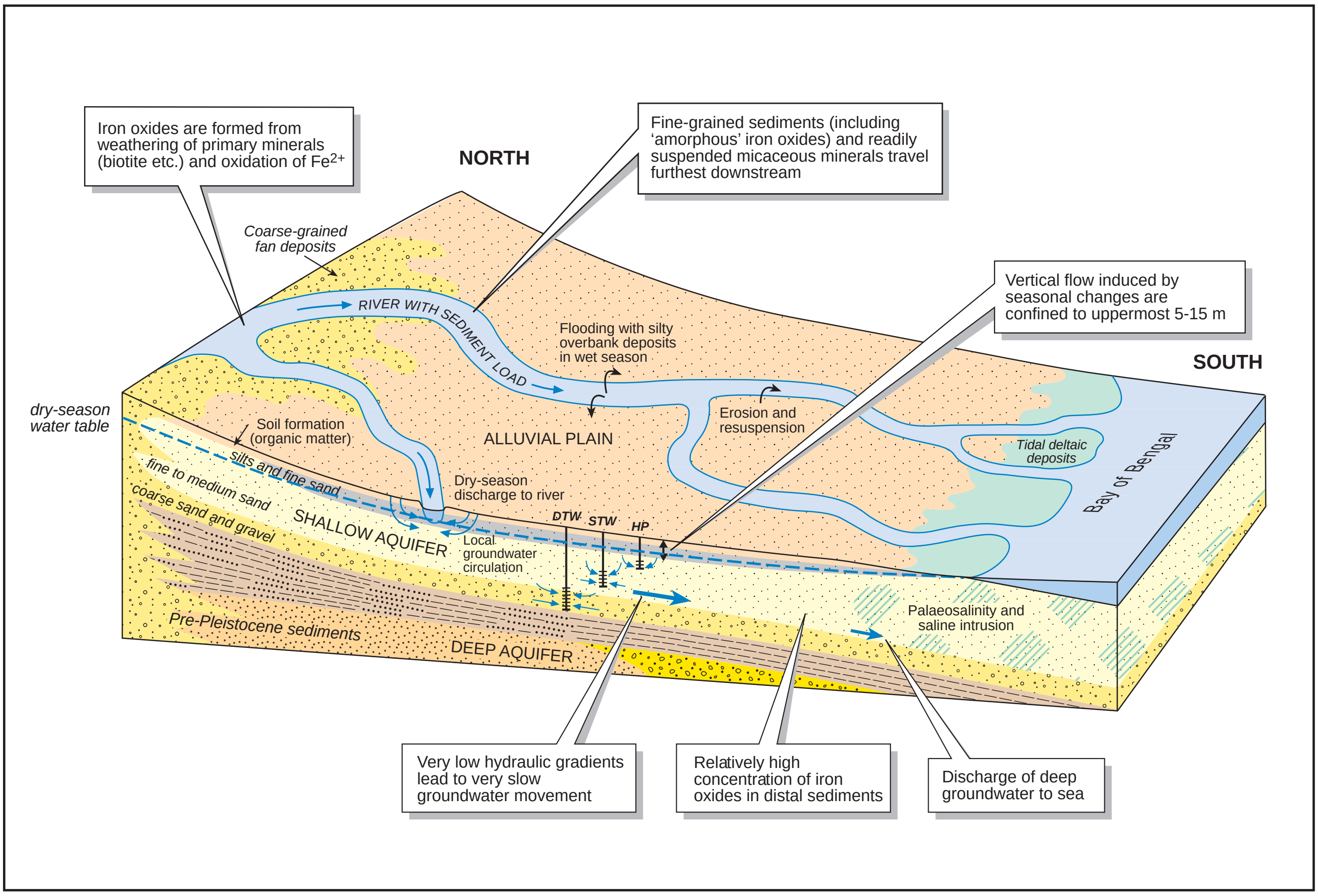

Figure 12.1. Block diagram showing the basic geology and hydrogeology of the Bengal Basin.

12.1.2 Source of the arsenic in Bangladesh groundwaters

Nature of the sediments

The following hypothesis provides a plausible explanation of many of the features observed in the groundwaters of the Bengal Basin. We stress that this is only a hypothesis and needs more data and more detailed studies to confirm it. The hydrogeological processes envisaged are shown in Figure 12.1 and the basic geochemical processes leading to arsenic release are summarised in Figure 12.2.

Others have speculated that the high concentrations of arsenic in the groundwaters of the Bengal Basin are due in some way to an exceptionally large source of As in the rocks somewhere upstream of the problem areas, but this does not appear to be the case. Indeed, the very large area affected, which includes sediments derived from all three of the major rivers of Bangladesh, indicates that there can be no single discrete source of the arsenic. The very large quantity of As involved also points away from a single source. It would have to be very large. Rather we believe that the sediments and their source rocks are typical of such alluvial and deltaic environments. There will of course be some source rocks, and particularly some minerals, with larger than average As contents, but this is normal and we can find no evidence that this is a critical factor in the development of high As groundwaters in the Bengal Basin (unlike the case in mining areas).

Indeed, no unusual high-arsenic source, such as a mineralised area, needs to be invoked since the release of only a small fraction of the arsenic from the solid phase to groundwater is sufficient to give rise to arsenic concentrations in excess of 50 μg L^{-1}. The primary attention should therefore be focused away from attempting to locate a unique, upstream source towards the geochemical and hydrogeological processes involved in the release of As from the sediments and the subsequent transport of As – or lack of it – within the aquifers. This will need to include a detailed characterisation of the nature of the labile As within these sediments including its sorption behaviour. The important sediment factors are likely to be rather more subtle than revealed by bulk chemical analyses.

The iron oxides are believed to be critical in Bangladesh. These are common secondary minerals formed by the weathering of iron-containing primary minerals. The large concentration of fresh biotite in many Bangladesh sediments provides a ready source of such iron. The rate of weathering of biotite is greatest under oxidising conditions since the mineral structure is destabilised by the oxidation of structural Fe^{2+}. The weathering in river sediments and soils is therefore likely to be particularly important for liberating iron.

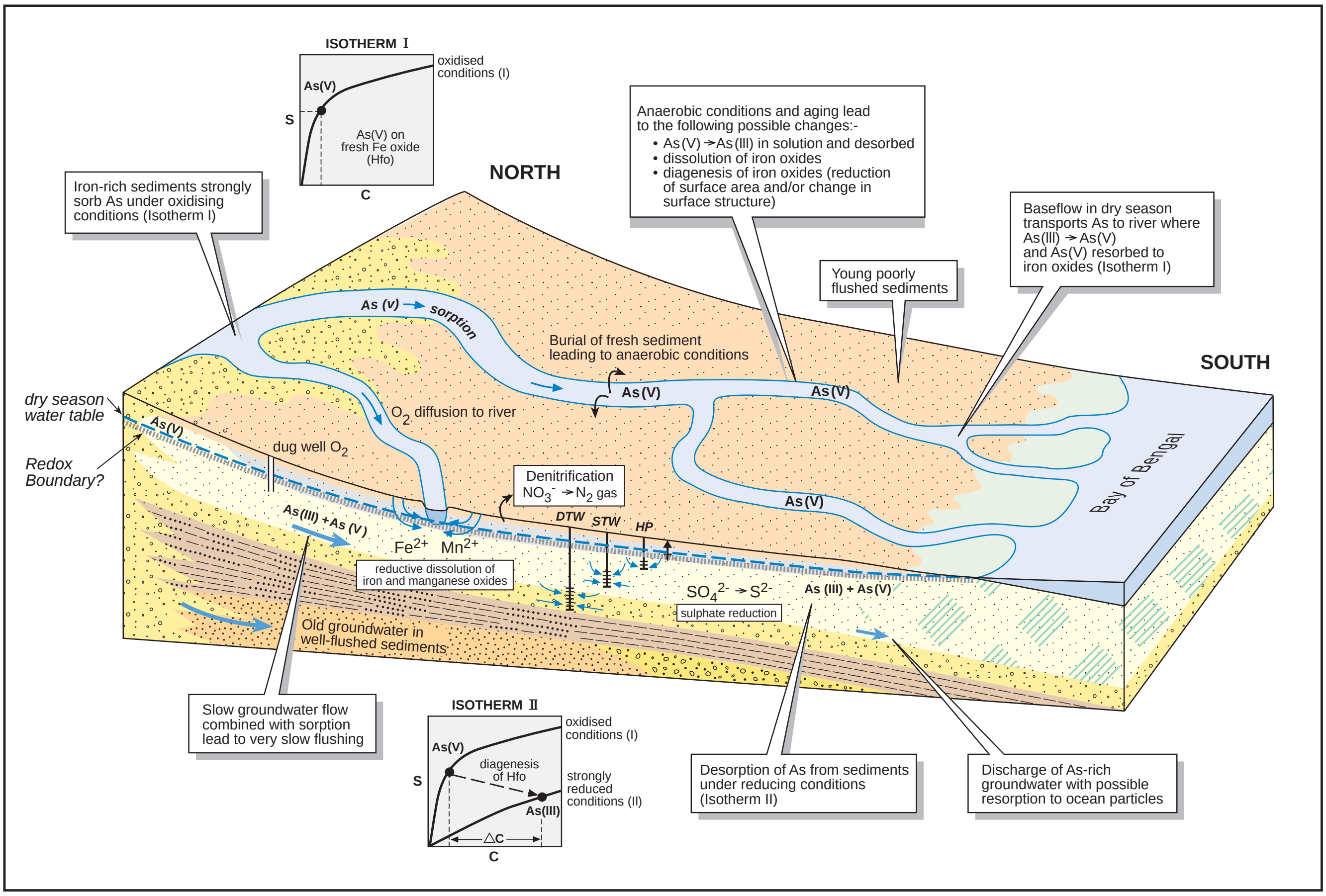

Figure 12.2. Block diagram showing the principal geochemical processes involved in the development of arsenic-contaminated groundwater in the Bengal Basin.

Iron oxides as a source of labile arsenic

'Labile As' is the As that can readily move reversibly from the sediment phase to the groundwater, and vice versa, given appropriate environmental conditions. It is distinct from 'non-labile As' found within the structure of minerals which has no possibility of being released rapidly because it requires the dissolution of the mineral or some very slow diagenetic reaction. This distinction is not 'black-and-white' but is nevertheless useful. Sorbed As tends to be labile because it is located at the mineral surface. Iron(III) oxides are a good source of labile As, because they often have a very large specific surface area and a high capacity and strong affinity for sorbing As. They are also unstable in reducing environments, in highly acidic environments and to a lesser extent, wherever there are large concentrations of chelating agents, particularly 'humic acids', which can lower the Fe^{3+} activity and promote dissolution.

Iron oxides in soils and river sediments scavenge arsenic from the soil solution and from river water building up a store of sorbed arsenic. The arsenic in river water is likely to be mostly present in its oxidised form, As(V), and in oxidising environments, this is very strongly sorbed by iron oxides. Typical concentrations of As in Bangladesh rivers and soil solutions are not known, but if they are typical of other areas in the world, can be expected to be of the order of 1 μg L^{-1} (Smedley and Kinniburgh, 2001). Even with just 1 μg L^{-1} As(V) in solution, the amount of arsenic sorbed by the iron oxides is relatively large. This can amount to several thousands of mg As kg^{-1} or ppm on an iron oxide basis.

The iron oxides are very fine-grained, colloidal in size, and are concentrated by the normal fluviatile processes in the fine-grained sediments. Natural sedimentological processes will mean that there will be some areas with higher-than-average concentrations of iron oxides than others, especially in those places where fine-grained deposits tend to have accumulated. Sometimes this will be in the predominantly sandy (aquifer) horizons. Relatively high concentrations of fine-grained sediments, including iron oxides, are deposited in the low energy part of the delta in south-eastern Bangladesh.

As the sediments are buried during the normal development of the delta, they rapidly become reducing owing to the microbial consumption of oxygen during the process of organic matter oxidation. This is facilitated by the presence of fresh organic matter from buried soils and the relatively high ambient temperature, about 28°C. Only small amounts of solid organic matter are required to reduce the available dissolved oxygen, nitrate and sulphate to trace concentrations. There is overwhelming evidence that most of the arsenic-affected Bangladesh groundwaters are reducing, and often strongly reducing. While occasional peat layers are found in Bangladesh sediments and these may facilitate the development of strongly-reducing conditions, there is no evidence that such concentrated sources of organic matter are required in order to produce reducing conditions. Organic matter, albeit at low concentrations, is widely disseminated in Bangladesh sediments. Much of this is likely to be relatively young (on geological timescales) and reactive.

Fine-grained overbank deposits of at least several metres thickness are present over much of Bangladesh and these surficial deposits, combined with the generally high water table, limit the diffusion of oxygen to the underlying sediments. Strongly reducing conditions and As release appear to be established within 5–10 m of the redox boundary. While the exact location of the redox boundary is unknown, it is probably just below the water table which is a few metres below ground level (bgl) in southern Bangladesh to some 5–15 m bgl in northern Bangladesh. The redox boundary probably shifts seasonally in response to the change in water level.

When the sediments become reduced, a series of geochemical reactions occur that lead to the release of some of the arsenic into the groundwater. The exact processes involved are not yet well understood but are likely to involve one or more of the following: (i) reduction of strongly adsorbed As(V) to maybe less strongly bound As(III), leading to the overall release of arsenic; (ii) iron (III) oxides partially dissolve and release iron as well as coprecipitated and adsorbed arsenic (and phosphate); (iii) the iron(III) oxides undergo diagenetic changes leading to the desorption of adsorbed arsenic. We collectively describe these processes as the *iron oxide reduction hypothesis*. A more detailed discussion of these is given below.

While the dissimilatory reduction and dissolution of iron oxides undoubtedly releases some arsenic, the As/Fe ratio observed in tubewell water is frequently greater than that found in the solid phase implying either that the dissolution is incongruent or that other processes such as desorption of As or precipitation of an Fe-mineral are operating. Desorption releases arsenic without any concomitant release of iron while iron sulphide or iron carbonate precipitation will reduce the concentration of soluble iron. Movement of groundwater will also tend to uncorrelate the released As and Fe as a result of chromatographic separation. Therefore a combination of mineral dissolution, precipitation, desorption and transport can provide a wide range of As/Fe ratios in groundwater and it is difficult to deduce much simply from the As/Fe ratio in groundwater. It is also likely that the overall As/Fe ratio released will change as the extent of dissolution increases.

If the iron oxide reduction hypothesis is correct, then the greater the iron(III) oxide concentration in the original sediment, particularly of the more bioavailable Hfo-type, then the greater the potential for the later release of arsenic to groundwater will be. Young, iron-rich sediments are therefore expected to be the most likely to provide sources of high-arsenic groundwaters. However, these waters need not necessarily be high-iron groundwaters. It is possible for desorption of As to occur from iron oxides with little or no release of iron although some exchangeable Fe^{2+} may be released. The solubility of iron oxides is in turn controlled by their bioavailability and their solubility product rather than by the amount of iron oxide present.

Therefore reductive desorption is different from reductive dissolution in terms of the expected ratio of As/Fe released. This may account in part for the wide range of As/Fe ratios seen in Bangladesh groundwaters. In practice, under reducing conditions, dissolution and desorption are likely to occur simultaneously and a range of availability and solubility of the various forms of iron oxides means that the dissimilatory iron-reducing bacteria (DIRB) will utilise the most soluble (most amorphous) oxides first. These kinetic factors may also introduce some dependence of dissolution on the initial quantities of the various iron oxides present.

12.1.3 Why is the deep aquifer low in arsenic?

As well as the release of As in the shallow aquifer, we have to explain why the deeper aquifer is low in As, usually very low. This will become much clearer when detailed studies of the variation of pore water chemistry and the associated sediment chemistry at different depths become available. Two possible explanations are: (i) *non-flowing system*: there is an increase in the As sediment-groundwater partition coefficient for some reason (e.g. change in redox status, change in surface chemistry), such that some of the As in the pore water is either readsorbed or was never released in the first place. The total amount of As in the sediment plus pore water system does not change, just its partitioning; (ii) *flowing system*: As is steadily flushed from the aquifer by fresh (low-As) groundwater. The rate of flushing in the past is likely to have been greater than at present (see below). These two possibilities are not mutually exclusive.

The frequent observation of As peaks in ocean and lake sediment pore-water depth profiles (Smedley and Kinniburgh, 2001) suggests that there could be a process that reduces the As concentration in deeper, older sediments that is not related to pore water flushing since the hydraulic gradients in such situations are unlikely to be favourable for extensive flushing. Some kind of slow geochemical (e.g. redox) or diagenetic (mineral) reaction may be operating. At present, there are few indications to be more specific.

There is also the possibility that the Dupi Tila sediments never contained large amounts of organic matter and that in any case, as the sediments became older, their labile organic matter content decreased and they became less able to maintain strongly-reducing conditions.

It is therefore possible that the brown, oxidised sediments often found at depth may never have been strongly reduced and that desorption of arsenic due to the various reductive processes may not have occurred to a significant extent. In other words, the most important drivers for arsenic release seen in the Holocene sediments may have not been operating. There are grey (reduced) sediments at considerable depth that give low-arsenic groundwaters, as in our deep well (LHTW7) and 150 m deep piezometer (LPW6) in Lakshmipur. However, while this groundwater was still reducing, it was less strongly reducing than the shallow groundwaters.

12.2 Transport of arsenic in Bangladesh aquifers

12.2.1 Introduction

There must be a relationship between the concentration of arsenic in groundwater and the groundwater flow since it is not possible to maintain a high concentration in groundwater in the face of high flows over a long period.

While the principles of solute transport in aquifers are quite well understood, very little is known about how rapidly arsenic actually moves through Bangladesh aquifers, or indeed in most alluvial and deltaic aquifers elsewhere in the world. Historically, there has been little need for such detailed and difficult-to-obtain information. This highly variable sedimentology of the Bangladesh aquifers and the uncertainties in the way in which groundwater has moved through the aquifers in the past, and is doing so at present, add to the complexity (Chapter 5). There is also a general lack of understanding of how arsenic binds to alluvial sediments in anoxic environments. The rate of arsenic transport is a result of the combination of the rate of water movement and the retardation brought about by sorption.

The rate of water movement and flow patterns will be influenced to some extent by the amount of pumping, especially by large-capacity irrigation pumps (Chapter 5). Therefore present flow patterns are not necessarily a good guide to past flow patterns or future flow patterns. It is clear from the large vertical and lateral variations in water chemistry, including salinity, that mixing in the aquifers has been limited. Indeed, this is characteristic of many of the high-As aquifers in the world. This points to highly stratified aquifer properties and/or sluggish groundwater movement.

It is clear from the simple calculations of groundwater flow made earlier (Chapter 5) that under past flow conditions it could have taken some 2,000–6,000 years to move one pore volume of water through the most permeable parts of the shallow aquifer, and several times longer for less permeable horizons. This is on a similar timescale to the age of the sediments indicating that, at most, just a few pore volumes of water have already been flushed through the shallow aquifer. Certainly the normal processes of groundwater flow will tend to slowly flush the arsenic and other mobile solutes out of the aquifer. Salinity will be the first component to be flushed (the 'salt' front) followed by the weakly sorbed ions, and then the more strongly sorbed ions (the retarded fronts). Slowly, the dissolved oxygen and nitrate in the influent water will tend to oxidise the sediment and the groundwater will tend to become less reducing, and eventually even oxidising. Some of the arsenic will return to the river as baseflow and will be re-oxidised and readsorbed onto the iron(III) oxides in the sediments. The sediment will gradually move downstream with the sediment load of the river, and some of it will ultimately be buried in the Bay of Bengal. This gradual oxidation process may involve reoxidation of the sediment iron(II) and increased adsorption of dissolved arsenic in a reversal of the original desorption and dissolution process. This process is likely to take hundreds of thousands of years.

Other groundwater will take a deeper flow pattern and may be discharged directly into the Bay of Bengal. Over thousands of years, the arsenic will slowly be flushed away or readsorbed and the Bangladesh aquifers will become good sources of potable water. The flushing is particularly slow because of the low hydraulic gradients in the delta. The sealevel was much lower during the last glacial period several thousand years ago and so flow to the sea was then much faster. This will have helped to flush the arsenic out of the older and deeper sediments. The much longer history of flushing in the deep aquifer may explain why it is now practically arsenic-free in many places. These deeper, older sediments are often oxidised (brown in colour) especially the Dupi Tila sediments, and have been through this reduction-oxidation change perhaps shortly after deposition.

The rate of flushing of arsenic from the aquifers therefore depends on the extent of groundwater flow (present and historic), the chemistry of the recharge water and the strength of sorption of the arsenic to the sediments. This may change with time as a result of sediment diagenesis.

With much deeper and older sediments, the extent of flushing will have been correspondingly greater and may have been sufficient to have flushed significant amounts of arsenic from the aquifer. However, another important factor also comes into play. The sea level at present is as high now as it has been for the last 120,000 years. Only 20,000 years ago, during the maximum of the last glaciation, the sea level was some 130 m lower than at present. This would have led to much lower water tables, deeper unsaturated zones and greater hydraulic gradients. Therefore the rate of movement of groundwater would probably have been greater although the greater gradient must be offset against the drier climate then prevailing – the monsoon was not operating. The lower water table may have meant that the sediments never became strongly reducing.

The speed with which arsenic is flushed from the aquifer will depend in part on the arsenic sorption isotherm. Some detailed transport calculations for arsenic were carried out earlier (Volume S3, DPHE/BGS/MML, 1999) using various assumptions about the arsenic sorption isotherm. These calculations were indirectly based on the diffuse-layer model of Dzombak and Morel (1990) and were based on the assumption that some kind of iron oxide analogous to hydrous ferric oxide (Hfo) was present in the sediment. In fact, as discussed earlier, it is possible that the iron oxides present in the reduced sediments are significantly different from Hfo. However, the critical feature is the adsorption isotherm with its implied retardation.

A wide range of isotherms was used in these preliminary transport calculations (DPHE/BGS/MML, 1999) because low- and high-Fe sediments were considered as well as low and high groundwater phosphate concentrations. Phosphate was included as a competitor and it is quite likely that this overestimated the true competitive effect thereby compensating to some extent for the possible overestimation of sorption by the iron oxides. Retardation factors vary with concentration because of the nonlinearity of the isotherms but were typically estimated to be 5–100 L kg^{-1} for arsenite and 5–1000 L kg^{-1} for arsenate (DPHE/BGS/MML, 1999).

12.2.2 Sorption of arsenic by sediments

There is a considerable amount of information about the interaction of arsenic with iron(III) oxides and other model oxide compounds but it is not yet clear how this relates to Bangladesh sediments. The greatest uncertainties lie in the nature of the solid phases present in the sediments, and from a sorption point of view, the nature of the As sorption isotherm for these phases, and their sensitivity to variations in groundwater quality. The presence of other major and minor ions in groundwater can both increase and decrease As sorption but it is expected that the competitive interactions leading to a reduction in As sorption are most likely to predominate.

The amount of arsenic adsorbed is highly dependent on many aquifer and groundwater parameters. These need to be understood in order to provide reliable predictions. The necessary theory for the competitive sorption of anions such as $As(V)O_4^{3-}$, $As(III)O_3^{3-}$, PO_4^{3-}, and HCO_3^-, is complex and critical laboratory data need to be gathered and appropriate models and thermodynamic databases developed.

Two broad approaches aimed at achieving a better understanding of the transport of solutes such as arsenic in aquifers are possible: (i) *laboratory-based approaches* – the sorption isotherm is measured in the laboratory using batch equilibration or column breakthrough experiments and these results are combined with a water flow model to predict field-scale transport; (ii) *field-based approaches* – the movement of arsenic (and other solutes) is measured in the aquifer using tracer tests or some other form of monitoring and the results fitted to the appropriate transport equations. The first approach has the disadvantage that of itself it says nothing about groundwater movement (which is itself difficult to characterise); the second approach overcomes this problem to some extent, but usually requires highly accelerated flow rates to make the changes observable within a short timescale and it does not provide a fundamental insight into how the transport might change under different groundwater flow or quality conditions or with different sediment characteristics. The best strategy is probably therefore a combination of the two.

The laboratory approach is particularly difficult for Bangladesh sediments since the sediments are reducing and will significantly change their sorption (and hence transport) properties when oxidised on exposure to air. Sediments would therefore have to be protected from oxidation as soon as they are retrieved from the aquifer. Such techniques have been quite widely used elsewhere, for example when studying marine sediments, but it was not possible to adopt such techniques within the scope of this project. Others are presently carrying out such detailed studies in Bangladesh (Foster et al., 2000).

Therefore while the mineralogical studies undertaken on Bangladesh sediments within this study (Chapter 11) are of value in defining the overall mineralogy and chemical composition of the sediments, they do not provide a sound basis for establishing the sorption and transport properties of the sediments. The ammonium oxalate extracts of sediments described in Chapter 11 give some indication of the concentration of iron oxides and other relatively soluble minerals, and an upper limit on the amount of 'labile' arsenic present. These data are also far from ideal for sorption modelling but help to constrain the modelling to some extent.

12.3 Modelling arsenic sorption by iron oxides

12.3.1 The sorption isotherm for iron oxides

The sorption isotherm describes the relation between the concentration of arsenic in the sediment and the concentration in the groundwater. It defines the extent to which the solid phase buffers dissolved solute concentrations and the slope of the isotherm is directly related to the retardation experienced by the solute during groundwater flow (Appelo and Postma, 1994). Judging from work on other sediments and pure minerals, particularly oxide minerals, the form of the isotherm is likely to depend on many factors including the nature of the sediments and the chemistry of the groundwater, including pH, arsenic concentration and speciation, and to a lesser extent the concentrations of phosphate, silicate, bicarbonate, calcium, magnesium and iron.

The classic and idealised sorption isotherm is the Langmuir isotherm. This is characterised by a linear isotherm at low concentrations where the probability of a solute adsorbing to the surface is directly related to its concentration in solution. At higher concentrations, there is a greater possibility of the solute hitting an already occupied surface site which leads to a reduced isotherm slope with an eventual flattening out as most sites become filled and the probability of hitting an empty site becomes very low. This plateau at high concentrations gives an estimate of the number of sorption sites. In practice, sorption of charged solutes (ions) on oxides normally does not follow this simple model because as the ions are adsorbed, they change the surface charge appreciably. Normally this makes further adsorption more difficult and results in an increase in the curvature (nonlinearity) of the isotherm. Electrostatic effects are very important for controlling the interaction of ions on oxide surfaces and describing these interactions forms the basis of most so-called 'surface complexation' models. Also, oxide surfaces can be intrinsically heterogeneous which will also lead to additional nonlinearity.

Iron oxides have a very strong and well-documented affinity for arsenic, particularly As(V), but at high pH ($pH>9$), As(III) sorption can exceed that of As(V). Indeed, the strong sorption of As(V) is the basis for many methods of removing arsenic in water treatment. In our earlier report (DPHE/BGS/MML, 1999), we estimated sorption isotherms for As(V) and As(III) based on the assumption that the arsenic was adsorbed to iron oxides which could be approximated by hydrous ferric oxide (Hfo). The iron oxide content of some Bangladesh sediments was estimated by an ammonium oxalate extraction. These hypothetical isotherms were then linked to a standard groundwater flow model to provide estimates of the rate of arsenic movement in typical Bangladesh aquifers subject to a range of constraints.

In modelling the sorption of As by Fe oxides, the type of iron oxide chosen is important. The iron oxides present in Bangladesh sediments have not yet been well characterised and while this could include Fe(III)-oxides such as Hfo, goethite (α-FeOOH) or hematite (α-Fe_2O_3), it is also likely to include various mixed-valence oxides such as magnetite (Fe_3O_4) and possibly a green rust (e.g. $Fe(III)_2Fe(II)_4(CO_3)(OH)_{12}.nH_2O$) (Taylor, 1980; Génin et al., 1998). In the laboratory, dissimilatory iron-reducing bacteria (DIRB) such as *Shewanella putrefaciens* have been shown to reduce Hfo to various Fe(II)-containing minerals including siderite ($FeCO_3$), vivianite ($Fe_3(PO_4)_2$), fine-grained magnetite and a green-rust type compound, depending on conditions (Frederickson et al., 1998). Sulphate-containing green rusts have been most widely studied (Hansen and Poulsen, 1999) but are not likely to be the dominant form in Bangladesh because of the generally low sulphate concentrations. Heron et al. (1994) found that most of the 0.5M HCl-extractable iron (= FeS, $FeCO_3$ and '$Fe(OH)_3$') in the sulphate-reducing part of a sandy aquifer in Denmark was present as Fe(II) not Fe(III).

The arsenic-affected sediments are often dark grey in colour (when wet) and the small amount of colloidal material sometimes found when filtering the groundwaters usually has a grey-green colour characteristic of reduced Fe minerals. Bicarbonate-stabilised green rusts are therefore a possibility. The surface chemical properties of such oxides are not known.

Most of the sorption data in the literature is for the Fe(III) oxide minerals: Hfo, goethite and hematite. There is very little information for magnetite, for example, although its point of zero charge is believed to be about pH 6.5, some 1.5–3 pH units lower than for the Fe(III) oxides.

It is a major exercise to characterise all the surface interactions of importance, especially for redox-sensitive minerals, and developing general chemical models of such interactions on oxides is an active area of research. The iron oxides found in Bangladesh may be very fine-grained (colloidal-sized) and may therefore not be easily visible or characterised by traditional mineralogical techniques. Many are probably present as coatings. Significantly, acid ammonium oxalate is known to partially extract non-Hfo forms of iron oxide (such as magnetite, akageneite and green rusts) and so there is necessarily much uncertainty as to the exact form of the iron oxides extracted (Heron et al., 1994; Kostka and Luther, 1994). It is also known that in reducing sediments, acid ammonium oxalate may be able to partially dissolved crystalline iron oxides since Fe^{2+} is known to catalyse the dissolution of these iron oxides (Heron et al., 1994). It will also displace exchangeable Fe^{2+} but this is expected to be relatively small. Judging by the amount of magnesium and aluminium dissolved (Chapter 11), it is also likely to dissolve some clays.

Nevertheless, since sorption reactions are likely to play a role in the groundwater arsenic problem in the Bengal Basin (and elsewhere), it is useful to explore at a semi-quantitative level some of the important features given our current level of understanding. We suspect that the iron oxides are the most important oxides in Bangladesh sediments because of their relative abundance and because the geochemical associations observed with arsenic tend to be stronger for iron than for manganese or aluminium.

12.3.2 Arsenic sorption by hydrous ferric oxide (Hfo)

Existing models

Below we use Hfo as a 'model' iron oxide for some example sorption calculations but we do not want to imply by this that Hfo is necessarily the only, or even the main, form of iron oxide in Bangladesh sediments. Hfo has the advantage that it has been widely studied and there is a readily-available thermodynamic database for many of the key reactions and so is easy to model (approximately). It is likely that many of the interactions shown by Hfo will also be shown by other oxides albeit to a quantitatively different extent.

Dzombak and Morel (1990) critically reviewed the sorption data for a wide variety of cations and anions by hydrous ferric oxide (Hfo) and fitted the results to a simple model, the diffuse layer model (DLM). More sophisticated models have also been proposed, of which the most successful is the CD-MUSIC model of Hiemstra and van Riemsdijk (1999). However, a comprehensive database of model parameters for the CD-MUSIC model is not yet available. Therefore while the DLM undoubtedly has limitations, especially when it comes to modelling competitive interactions, it is probably sufficiently accurate to provide a semi-quantitative insight into the scale of the interactions that are likely to be found.

The DLM and the accompanying database have been included in a number of general-purpose geochemical speciation programs including PHREEQC, the Geochemist's Workbench, ECOSAT and MINTEQA2. There was not much arsenic sorption data available for Hfo in 1990 when Dzombak and Morel published their compilation, and the data from the principal datasets available then showed some inconsistencies. However, subsequent measurements of As(V) and As(III) sorption by Hfo (Wilkie and Hering, 1996) have shown that the published database and model are reasonably reliable, and probably sufficiently good for making initial estimates of sorption by Hfo.

Therefore below we present some model calculations to demonstrate the basic features of As sorption by Hfo. We used PHREEQC (Parkhurst and Appelo, 1999) and ECOSAT (Keizer and van Riemsdijk, 1998) for our calculations. These calculations are for a pure Hfo-As system with a background electrolyte of approximately 0.01M NaCl. In the calculations, the concentration of Hfo is expressed in terms of the total Fe concentration in the system (1 mg L^{-1} Fe as Hfo is equivalent to 1.60 mg L^{-1} Hfo).

Since an Hfo-like compound is produced when Fe^{2+} is precipitated during air oxidation, the calculations below also give a guide to the possible efficiency of As removal by 'passive' oxidation of Fe-rich groundwaters. This will depend to some extent on the ratio of As(III) to As(V) and the pH and concentrations of other ions present.

pH dependence

Given an initial As(V) concentration of 100 μg L^{-1}, the expected sorption or 'removal' of As(V) depends strongly on the pH and the total amount of Fe (as Hfo) present (Figure 12.3). As(V) is very strongly sorbed below pH 7 and decreases quite rapidly above that pH. The pH of the

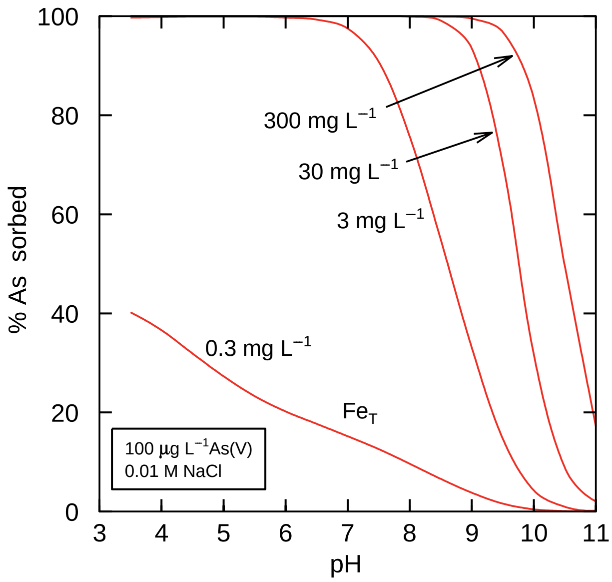

Figure 12.3. Calculated percentage of arsenic(V) sorbed by hydrous ferric oxide from a 100 µg As(V) L^{-1} solution as a function of the amount of Fe as Hfo present.

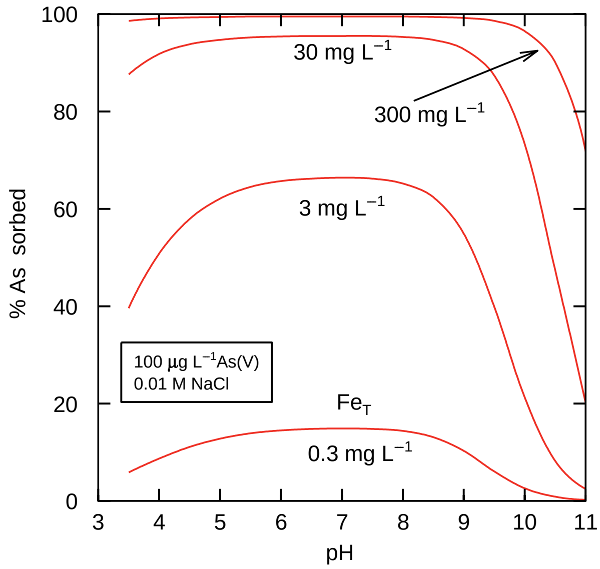

Figure 12.4. Calculated percentage of arsenic(III) sorbed by hydrous ferric oxide from a 100 µg As(III) L^{-1} solution as a function of the amount of Fe as Hfo present.

desorption edge depends quite strongly on the solid/solution ratio and so these pH's are not fixed – the higher the solid/solution ratio, the smaller the desorption at a given pH and the sorption edge shifts to a higher pH.

At the iron concentrations typical of Bangladesh groundwaters and used in arsenic removal plants (a few mg Fe L^{-1}), As(V) sorption decreases with increasing pH especially when the pH is above pH 7 and the As(V) concentrations are low. Therefore any upward shift in pH, especially above pH 7, could give rise to significant desorption of As from Hfo and in a closed system would result in an increase in As in solution. The magnitude of this shift depends on the solid/solution ratio. The position of the curves is also dependent on the total As concentration. The curves shift to a higher pH at lower As concentrations and are quite sensitive to uncertainties in the model parameters. However, at pH 7 and in the simple Fe-rich systems (those with more than 3 mg Fe L^{-1}), a significant amount of the As(V) should be sorbed on Hfo precipitated by the oxidation of the Fe(II).

The sorption behaviour of As(III) is quite different, especially the pH dependence (Figure 12.4). In particular, over the pH range 6–8, the sorption is independent of pH and depends primarily on the solid/solution ratio. At pH's and iron concentrations typical of Bangladesh groundwaters, As(III) sorption on Hfo precipitated during the oxidation of Fe^{2+} is likely to be only partial, and substantially less than for As(V). At high pH's (>pH 9), As(III) is more strongly sorbed than As(V). The sorption-pH curves have been calculated for 'simple' systems in the absence of other interacting ions. Strongly sorbed ions such as phosphate can have an important effect. This is shown in the adsorption isotherms at constant pH illustrated below.

Sorption isotherms at constant pH

Calculated As(V) adsorption isotherms at constant pH show that the isotherms depend strongly on the presence or absence of phosphate (Figure 12.5). In the absence of phosphate and above about 10^{-7} mol L^{-1} (7.5 µg As L^{-1}) As in solution, the isotherms at pH 6, 7 and 8 are approximately linear on a log-log scale with a slope of about 0.13. This indicates that the isotherms are very nonlinear (when plotted on a linear scale as sorbed amount against concentration) with the consequence that even at very low concentrations (a few µg L^{-1} or less) there is a considerable amount of arsenic adsorbed to the Hfo. For example, at pH 7 and an As(V) concentration of 10^{-9}M (equivalent to 0.075 µg As L^{-1}), the calculated amount of As sorbed is about 0.1 mol As kg^{-1} Hfo. This is equivalent to some 7500 mg kg^{-1} Hfo. At greater concentrations, the arsenic content of the Hfo is correspondingly greater. At pH 7–8, As(V) loadings can be as large as 1 mol kg^{-1} Hfo or some 75,000 mg kg^{-1}. Hfo therefore has both a large affinity and a large capacity for sorbing As(V) from natural waters. It should come as no surprise when iron oxide-rich sediments are found to contain large concentrations of arsenic.

The near-linearity of the isotherms on a log-log scale indicates that they can be approximated by a pH-dependent Freundlich isotherm. The high degree of non-linearity results from strong electrostatic interactions on the surface of the Hfo: as more and more As is adsorbed, the net negative charge of the oxide is increased, decreasing the surface potential (i.e. it becomes more negative) and leading to an increasingly unfavourable electrostatic environment for the sorption of more As.

The situation changes dramatically in the presence of phosphate. Phosphate competes very effectively with As(V) for sorption sites and reduces As(V) sorption greatly (Figure 12.5). The NHS showed that the median P concentration in As-contaminated shallow groundwaters

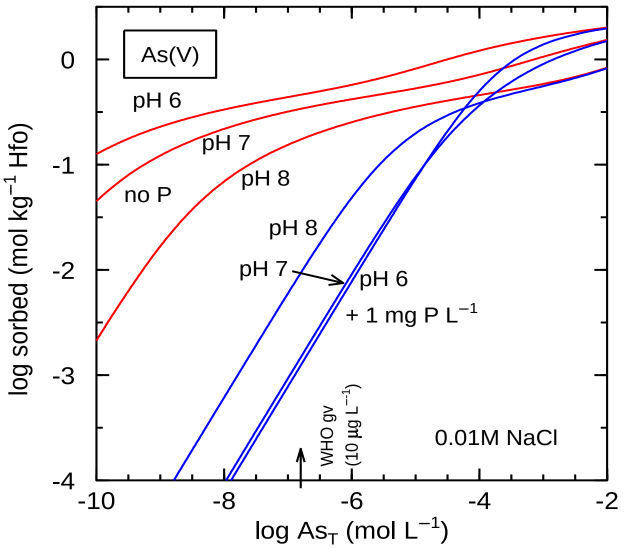

Figure 12.5. Calculated sorption of As(V) by Hfo as a function of As(V) concentration and pH in 0.01M NaCl background electrolyte. Calculated in the absence (red) and presence (blue) of an equilibrium dissolved phosphate-P concentration of 1 mg L^{-1}.

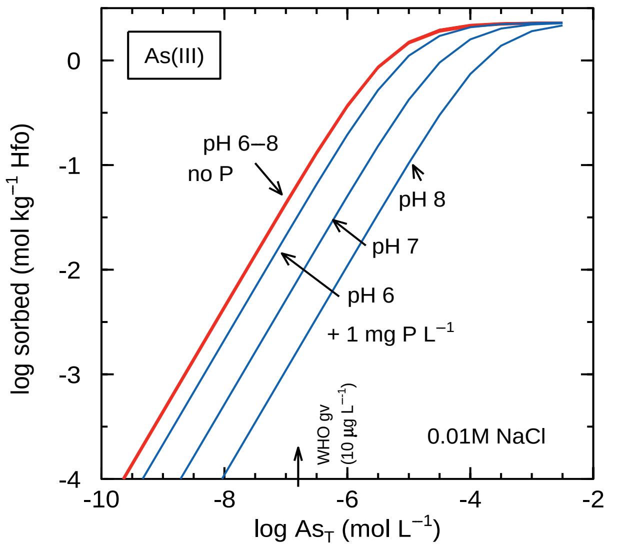

Figure 12.6. Calculated sorption of As(III) by Hfo as a function of As(III) concentration and pH in 0.01M NaCl background electrolyte. Calculated in the absence (red) and presence (blue) of an equilibrium dissolved phosphate-P concentration of 1 mg L^{-1}.

(greater than 50 µg As L^{-1}) was 1.1 mg P L^{-1}. We have therefore calculated the As(V) sorption isotherms for pH 6, 7 and 8 in the presence of an equilibrium (final) dissolved P concentration of 1 mg L^{-1} (3.23e-5 mol L^{-1}).

At low As(V) concentrations, the high As/P molar ratios mean that P outcompetes As very effectively and is calculated to reduce the sorption by one to three or more orders of magnitude (Figure 12.5). The isotherm is now linear at low As concentrations and is close to being a Langmuir isotherm overall. This is because the surface potential is now governed by the phosphate sorption and is essentially independent of the As(V) concentration over much of the isotherm. The pH dependence of the isotherms has been reversed from the no-P situation and there is a rather small pH dependence between pH 6–7. For typical groundwater As concentrations, increasing pH from 7 to 8 is calculated to increase As sorption slightly rather than decrease it.

As expected, the sorption isotherms for As(III) differ greatly from those for As(V) both in terms of the basic isotherms and the effect of phosphate (Figure 12.6). The plateau regions at near neutral pHs seen in Figure 12.4 (in the absence of phosphate) mean that As(III) sorption is essentially independent of pH in the region of interest for Bangladesh groundwaters, i.e. near neutral. This is confirmed in Figure 12.6 where the three isotherms are superimposed. The resulting pH-independent isotherm is nonlinear and conforms closely to a Langmuir isotherm. However, in the range of As concentrations relevant to most groundwaters, the isotherm has a slope of one on the log-log plot indicating a linear isotherm.

This difference in behaviour between As(V) and As(III) largely reflects differences in the importance of electrostatics. The dominant As(III) species in near-neutral pH solutions is the neutral H_3AsO_3 species and in the Dzombak and Morel (1990) model, this neutral species is the only form of As(III) sorbed. This sorption involves little change in surface charge. Hence, the conformity to the idealised Langmuir isotherm.

In the presence of 1 mg L^{-1} phosphate-P, the competitive effect is much less than for As(V) but As(III) sorption still decreases by up to an order of magnitude. The presence of phosphate has also induced some pH dependence with somewhat greater sorption at pH 6 than at pH 7 or 8. Comparing As(V) and As(III) sorption in the presence of 1 mg L^{-1} P, we can see that over the pH range of interest, As(III) is now calculated to sorb more strongly than As(V), the reverse of the situation in the absence of P. The situation is indeed complicated, and this is without considering HCO_3^-, SiO_4^{2-}, DOC, Ca^{2+}, Fe^{2+} and Mg^{2+}!

One interesting point suggested by this modelling is that in the presence of phosphate, the sorption isotherms for both As(V) and As(III) are essentially linear isotherms over the range of As concentrations typical of Bangladesh groundwaters (10^{-9} to 10^{-4} mol L^{-1}). If true, this greatly simplifies transport modelling since it implies that a simple 'Kd' or constant retardation factor approach can be used.

12.3.3 Desorption of arsenic from iron oxides and the formation of high-arsenic groundwaters

Anything that causes significant dissolution or precipitation of As-containing minerals or a change in the As sorption isotherm of the aquifer material will tend to be reflected by a mirror change in the As concentration of groundwater, i.e. desorption will lead to an increase in groundwater concentration, and *vice versa*. Both Fe(III) oxides and Fe(II) sulphide minerals are well-known scavengers of trace elements and so these are likely to be important minerals in this respect in Bangladesh in terms

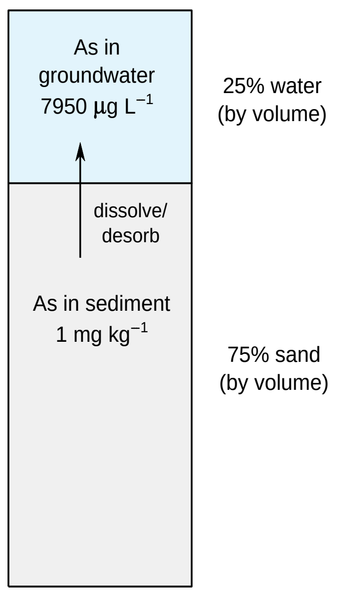

Figure 12.7. Schematic diagram showing how the consequences of a high solid/solution ratio on pore water arsenic concentrations. Complete dissolution of even small amounts of arsenic (1 mg kg^{-1} here) from a sandy Bangladesh aquifer sediment would give rise to extremely high concentrations of arsenic in the groundwater.

of dissolution/precipitation and sorption reactions. Clays may also be important.

Groundwater chemistry is particularly sensitive to any shifts in the sediment chemistry because of the very large solid/solution ratios found in aquifers (Figure 12.7). For example, assuming a porosity of 25% and a crystal density of the aquifer minerals of 2650 kg m^{-3} (typical of quartz) gives a solid/solution ratio of 7.95 kg L^{-1}; a porosity of 30% decreases this to 6.2 kg L^{-1} which is still very large. If an aquifer has a porosity of 25% and the sediment contains say 1 mg As kg^{-1} of labile As, the complete dissolution of that As would lead to a groundwater As concentration of 7950 µg As L^{-1}, far in excess of any drinking water standard. The oxalate-extractable As in Bangladesh sediments can exceed 1 mg kg^{-1} (see Table 11.14, Chapter 11) and while all, or even most, of this may not be labile, it demonstrates the sensitivity of the groundwater to changes in sorption. It only takes a small shift (less than 0.01 mg kg^{-1}) in the amount of labile As from the solid phase to the solution phase to give a significant groundwater As problem. These shifts are too small to be reflected accurately in 'total' sediment As determinations or even in oxalate-extractable determinations. Analysing sediments for total As is not necessarily a reliable indicator of a potential groundwater As problem.

From the calculations given above, groundwater pH increases in the presence of Hfo could provide one route for the formation of high As groundwaters. This is unlikely to be the driving force in Bangladesh since groundwater pH values are invariably near neutral. As discussed earlier, other processes giving rise to desorption of As are also possible (Table 12.1) and it is useful to explore some of these in a semi-quantitative way in order to estimate the magnitude of the changes expected and the relative sensitivity of these changes. The As-rich groundwaters frequently contain high phosphate concentrations and high bicarbonate concentrations, for example. It is often difficult to separate 'cause' from 'effect' since desorption reactions will result in the partial desorption (and increase in solution concentration) of many sorbed ions and so it can be difficult to identify the 'driving force' controlling the desorption reaction amongst the many correlated variables.

In order to make the calculations relevant to the Bangladesh situation, we assume the following scenario for the formation of high-As groundwaters. Many of the details are as yet unsubstantiated and so at present this is just a hypothesis but it is plausible and is consistent with existing data.

(i) Freshly-formed Hfo is formed in soils and in river sediments by the oxidative weathering of primary minerals such as biotite. As a result of soil erosion and the reworking of older sediments, this Hfo is slowly transported down the river. Formation of Hfo as opposed to the more crystalline iron oxides, will tend to be favoured because of numerous phases of precipitation and dissolution as a result of successive redox cycles following burial and exposure of the sediments. In this way, the iron oxides are constantly kept 'young' (McGeehan et al., 1998). Hfo tends to be most abundant in young soils and sediments and because it is colloidal in nature, will tend to be quite readily transported. It will therefore be concentrated in the lower parts of the delta, along with other fine-grained material.

(ii) While in the river bed, this Hfo sorbs As from the passing river water. We assume for the sake of the calculations that this As is present entirely as As(V) but this is unlikely to be strictly the case. As we have shown above, substantial amounts of As(V) can be accumulated on the sediment by sorption, even while the As concentration in the river water is small. This is a consequence of the high affinity of Hfo for As(V). The concentration of As in the river water will reflect the various As sources upstream, including mineralised areas, and the extent of adsorption by the upstream sediments. The river water will approach a steady state concentration of As. The pH of the river water will primarily depend on whether there are free calcium and magnesium carbonates in the sediments, on the effect of biological activity and the degree of reaeration. In Bangladesh, the river pH is probably about pH 7.5–8.0 (Datta and Subramanian, 1997) but could be lower in carbonate-free areas. The lower the pH, the greater the sorption of As(V) by the sediments is likely to be.

(iii) River sediment is continuously being deposited either as overbank deposits during times of flood or at the distal end of the delta as the delta advances. As soon as the sediment is buried, dissolved oxygen will be depleted from the pore water by microbial oxidation of the small amounts of fresh organic matter present in the sediments. When the sediment is buried beyond a certain depth, the rate of oxygen diffusion from the surface will be insufficient to maintain dissolved oxygen in the water and the pore water and sediments will become anaerobic. This change occurs at the redox boundary which in many natural environments is quite sharp. Further oxidation of

Table 12.1. Geochemical processes that can cause an increase of the arsenic concentration in groundwaters

Process	Comments
Solution complexation	Recent data suggest that carbonate ions form stable complexes with As(III) and As(V) in solution. This will lower the activity of free arsenic ions in solution and will tend to increase the solubility of any As minerals and cause the desorption of As from oxides. Both of these mechanisms will tend to increase the concentration of As in groundwater. Bicarbonate concentrations in many As-affected groundwaters are relatively high (compared with surface waters) as a result of the oxidation of fresh organic matter and the dissolution of carbonate minerals and so while this mechanism of arsenic release might be correlated with sediment burial and reduction, it does not require such reduction and could also occur in high bicarbonate groundwaters in oxidising environments – there can be a good correlation between arsenic and bicarbonate in such oxidising environments (Smedley et al., 2001a).
Reductive dissolution of iron oxides	Reduction of Fe^{3+} leads to the (partial) dissolution of Fe(III) oxides and the release of Fe^{2+}. This will lead to the co-release of both adsorbed solutes (including As) and structural (solid solution) components. Details of the mechanisms involved are not well understood quantitatively but the amount of co-release by pure (congruent) dissolution should be proportional to the amount of dissolution, i.e. to the release of Fe^{2+}. Dissolution (and As release) will continue until all the oxide has dissolved, with the least crystalline oxides dissolving first. Some of the released Fe^{2+} is readsorbed on iron(III) oxide surfaces. Specialised dissimilatory iron-reducing bacteria have been identified.
Reductive desorption due to reduction of As(V) to As(III) in solution	Since As(III) is less strongly sorbed than As(V) by oxides under near neutral pH conditions (Figures 12.3 and 12.4), the reduction of As(V) to As(III) may lead to the release of As. For iron oxides, this is independent of any Fe released as a result of mineral dissolution. Reductive desorption can also occur on aluminium oxides and clays. Once the system has adjusted to the new redox conditions, there should be no further As release, i.e. it is essentially a one-off process. There is as yet little experimental evidence to support this hypothesis directly and calculations suggest that there can be a reversal in the presence of other specifically adsorbed ions such as phosphate. Some recent laboratory results (Langner and Inskeep, 2000) demonstrate that reductive desorption does not necessarily occur rapidly. A different type of reductive desorption could also occur through the change in oxidation state of the structural Fe(III) ions (see below).
Competitive desorption of As(III) and As(V)	Anything that leads to an increase in the concentration of strongly sorbed anions such as phosphate, silicate and bicarbonate could lead to the desorption of As(III) and As(V) through competitive sorption reactions. This also applies to AsO_4^{3-} and AsO_3^{3-} competition. The most likely competitor anions in Bangladesh groundwaters are phosphate, bicarbonate (example calculations by CAJ Appelo, personal communication, 2000; www.xs4all.nl/~appt/co2_hfo.html suggest that bicarbonate-induced desorption could be important), silicate and dissolved organic matter (humics). Unlike the reductive dissolution of iron oxides, there will be no corresponding release of large quantities of dissolved Fe. Weakly-bound ions such as chloride and nitrate have little effect. These competitive desorption effects will be counteracted to some extent by any specific adsorption of multivalent cations. Ca^{2+}, Fe^{2+} and Mg^{2+} are the most likely candidates in Bangladesh groundwaters. Oxidation of organic matter can lead to increased concentrations of bicarbonate and phosphate while mineral dissolution can lead to increased bicarbonate, silicate and phosphate concentrations.
pH changes	An increase in pH will tend to lead to the desorption of As(V). As(III) sorption is little affected by pH changes at the pH of most groundwaters. The presence of competing specifically adsorbed anions will affect the pH dependence of sorption and the nonlinearity of the As isotherm – it tends to decrease the nonlinearity of the isotherm.
Diagenesis of iron oxides	Freshly-precipitated iron oxides are unstable and tend to crystallise with time. This invariably leads to an increase in particle size and a reduction in specific surface area, and probably a reduction in the number of sorption sites per unit mass. This could lead to the desorption of adsorbed solutes including any sorbed As. However, some ions may be incorporated as a solid solution into the evolving structure which will reduce the impact on solution concentrations. There may also be a change in crystal structure, generally an increase in structural order or 'crystallinity' say from ferrihydrite to goethite. This will also change the mineral surface structure and alter the sorption isotherm – this could lead to an increase or decrease in sorption through its impact on the intrinsic binding affinities (log K's). Some of these diagenetic changes have been observed in Atlantic ocean pelagic sediments from below the sediment redox boundary (Haese *et al.*, 1998).
Reduction of solid phase Fe(III) to Fe(II)	Another form of diagenesis found under reducing conditions is that some of the Fe(III) in iron oxides and other Fe(III)-containing minerals will be reduced to Fe(II). With oxides, this leads to a change in coordination of the Fe and is a precursor to the detachment of Fe(II) as part of the reductive dissolution process (Stumm and Sulzberger, 1992). The change in oxidation state is therefore likely to lead to a change in the surface structure of the iron oxides and a consequent change in the sorption isotherm for the (partially) reduced surface. It could increase or decrease sorption but electrostatic considerations suggest that a decrease in sorption is more likely because of the reduction in positive charge in the solid phase. This is consistent with the change in the point of zero charge of oxidised iron oxides which varies from about pH 8.1 for Hfo to about 9.5 for goethite while that of magnetite is about pH 6.5. Therefore, all other things being equal, a change from Hfo to magnetite could lead to a more negatively-charged surface and desorption of both As(III) and As(V). Solid state diffusion of electrons is relatively fast and so reduction of deeper-placed structural Fe(III) could also take place leading to minerals with a magnetite or green-rust structure. Ultrafine-grained authigenic magnetite has been identified in recent sediments and soils (Maher and Taylor, 1988). Fe(III) in other minerals, such as phyllosilicates, could also be reduced. This may be accompanied by a colour change and can be very rapid. Vermiculite rapidly changes colour from a light brown to a steel grey when reduced. This too affects the layer charge.

Table 12.2. Arsenic and major element chemistry of some Bangladesh rivers

Sample no.	Description	Longitude	Latitude	Date sampled	As_T	Na	K	Ca	Mg	Si	Fe	Mn	SO_4	P
					μg L⁻¹	mg L⁻¹								
9901552	R. Wabda, Mandari, Lakshmipur (M203)	90.8932	22.9110	26/11/99	1.0	12.2	2.3	4.0	4.7	0.9	0.22	0.055	0.7	<0.2
9901553	R. Meghna near Meghna bridge	90.7110	23.5304	22/11/99	<0.5	6.0	2.0	7.2	3.7	6.4	0.11	0.028	2.3	<0.2
9901554	Jamuna R. near Bangabandhu bridge	88.7530	24.0004	3/12/99	0.7	4.0	2.4	25.4	5.9	6.6	0.03	0.002	13.4	<0.2
9901555	R. Ganges, Rajshahi	88.5705	24.3622	2/12/99	1.8	13.9	7.9	36.4	10.3	7.2	<0.01	0.014	13.8	<0.2
9901556	R. Mahananda at Chanlai bridge, Nawabganj	88.2565	24.5994	2/12/99	2.7	15.0	2.7	22.1	5.9	15.8	0.06	0.046	4.6	<0.2
9900389	R. Mahananda at Chanlai bridge, Nawabganj	88.2537	24.5993	22/3/99	29	22.9	4.5	22.9	14.9	16.5	0.04	0.153	4.7	<0.2
9900414	Wapda canal, Kamalpur, Lakshmipur	90.8422	22.9040	3/4/99	1.7	0.9	8.0	0.9	23.3	7.4	0.09	0.036	46.1	<0.2

organic matter will lead to the reduction of nitrate to nitrite and ultimately to nitrogen gas (denitrification), formation of ammonium, and eventually to the reduction of sulphate to sulphide. The reductive dissolution of manganese and iron oxides will also occur with iron being released more slowly than manganese (Williamson et al., 1994). As a result, Fe(II)-containing minerals such as siderite ($FeCO_3$) or iron sulphides may form. The most readily 'available' iron oxides will be reduced first. The pore water pH will tend to be stabilised close to pH 7.

This change to anaerobic conditions will lead to the reduction of As(V) to As(III) both in solution and in adsorbed forms. The kinetics of these reactions are slow on laboratory timescales but probably not on geological timescales. At present, opinions vary about the degree to which the As(III)–As(V) couple is in redox equilibrium in groundwaters. This reduction could lead to desorption of As since As(V) is often, but not always, more strongly sorbed than As(III). A decrease in pH, say from pH 8 (river) to pH 7 (buried sediment), may also affect the sorption of As(V).

12.4 MODELLING THE DEVELOPMENT OF ARSENIC-RICH GROUNDWATERS

12.4.1 Approach

While it is too early to model the evolution of the arsenic-rich groundwaters in Bangladesh with much confidence, it is possible to carry out some simple modelling to show what might happen if the sequence of events described above takes place. We concentrate on the dissolution and desorption of As by iron oxides but qualitatively similar arguments could be applied to other oxides and clays. The key reactions appear to be between arsenic species and oxides or oxide-like minerals. While manganese oxides are significant for arsenic sorption and release in some environments, we have not seen any data that suggest this is true in Bangladesh.

The following parameters are assumed to change in the groundwater and aquifer following sediment burial: (i) pH (pH 8 to pH 7); (ii) phosphate increases in concentration (0.03 to 1 mg P L^{-1}); (iii) redox potential (oxidising to reducing) with As(V) changing to As(III); (iv) reduction in specific surface area of iron oxide (600 to 300 $m^2\ g^{-1}$ or less), and (v) reduction in As(III) binding affinity on the iron oxide (log K decreased by 1 or 2 units). The first three changes probably occur rapidly, the last two more slowly.

We have not attempted to model the entire evolution of the groundwaters at this stage. It is relatively straightforward to account for the development of the major-ion chemistry in terms of the oxidation of organic matter, reduction of sulphate, dissolution of carbonates, silicates etc. Rather we concentrate on how the As-rich groundwaters may have developed.

12.4.2 River water quality

Since we take as a starting point iron(III) oxide in equilibrium with river water, we need to know the average chemistry of Bangladesh river water. There are few As analyses of Bangladesh rivers but the indications and expectations are that it is generally low, especially in the major rivers. We analysed seven surface waters mainly collected from major Bangladesh rivers (including the Ganges, the Brahmaputra and the Meghna), mostly sampled during November–December 1999. This time of sampling corresponds to the early part of the dry season. The results (Table 12.2) show that, with one exception, the As concentration in the sampled river waters was less than 3 μg L^{-1} and in three cases was 1 μg L^{-1} or less. The most notable exception was for the River Mahananda which runs through the Chapai Nawabganj As hot spot area and in March 1999 had a concentration of 29 μg L^{-1}. However, a second sample taken from the same location in December 1999 gave an As concentration of only 2.7 μg L^{-1}, some ten times lower. It is not known why there was this large change, whether it is real or not, or in general how the surface water As concentration varies with river flow and time.

Most of the samples were from large rivers, some very large rivers, and had correspondingly large flows. Concentrations in small rivers and near-stagnant ponds may be different and more variable. The As speciation was not determined in the river water samples. We assume for the sake of the modelling a river water As concentration of 1 μg L^{-1} and that all of this is present as As(V). We have not studied any modern river sediments in the laboratory.

12.4.3 Sorption of arsenic by river sediments

Calculated arsenic loading of the active river sediment

While the CD-MUSIC model of Hiemstra and van Riemsdijk (1999) is the most promising of the oxide adsorption models presently available, there is as yet no database for Hfo-cation and anion interactions available. The CD-MUSIC model is available in ECOSAT (Keizer and van Riemsdijk, 1998) and ORCHESTRA (Meeussen, 2000) but not in PHREEQC. Some preliminary calculations trying to fit the existing Hfo-As experimental data to CD-MUSIC were carried out but these brought up too many inconsistencies in the experimental data to make the results usable within the scope of this project.

In the following calculations, we assume that a fraction of the extractable iron in Bangladesh river sediments behaves like Hfo and that this fraction interacts with arsenic and other ions according to the Dzombak and Morel (1990) diffuse layer model. The model itself, and the way in which it accounts for competitive interactions (Wilkie and Hering, 1996), involve many important simplifications that have not been verified over the wide range of conditions required. Indeed it is likely that some of the assumptions will be subsequently be shown to be incorrect. The results must therefore be viewed with caution. The modelling has been carried out to give a first guide as to the order of magnitude of the interactions expected and to guide further modelling and data collection.

We assume that an average sediment has a crystal density of 2650 kg m^{-3}, a water-filled porosity of 25% and contains 0.2% Fe_{ox} (2 mg Fe_{ox} kg^{-1} sediment), an oxalate-extractable Fe content typical of that found in the Faridpur sediments (Figure 11.14). This is equivalent to 3.19 g Hfo kg^{-1} sediment or 25.4 g Hfo L^{-1} of groundwater. If we further assume that the river water has: a pH of 8.0; a dissolved phosphate-P concentration of 0.03 mg L^{-1}; a dissolved As(V) concentration of 1 μg L^{-1} and an ionic strength of 0.05 mol L^{-1}, then using Dzombak and Morel's default parameter values, the Hfo will have an As(V) loading of 34 mmol kg^{-1} Hfo or 8.2 mg kg^{-1} sediment. This is about an order of magnitude greater than the observed As_{ox} concentrations of about 0.5–2 mg kg^{-1} in the depth range 15–50 m (Figure 11.13). The river PO_4–P concentration is probably less than 0.03 mg L^{-1} but this value compensates to some extent for the omission of bicarbonate and silicate competition (Swedlund and Webster, 1998).

We can reduce the calculated sediment loading with As by reducing either the sediment iron concentration or the river As concentration, or by converting some or all of the As(V) to As(III) or by increasing the river phosphate concentration. Here we assume that only 10% of the oxalate-extractable Fe is present as an Hfo-like oxide since it is known that oxalate overestimates Hfo-like material in reduced sediments. Clearly, this is an important and somewhat arbitrary assumption.

With this reduced Fe oxide concentration, the As loading of the sediment is reduced accordingly and is now plausible. More than 99.9% of the arsenic in the system (adsorbed plus solution) is adsorbed. The high value used here for the ionic strength (made up from NaCl) and throughout these simulations meant that small differences in ionic strength had little influence on the results. While changes in ionic strength do have some effect on As sorption, the effect is relatively small and should be included later when a more complete model of all the major changes in groundwater chemistry has been derived.

This river sediment with the above adsorbed arsenic load is assumed to be buried, after which various changes occur. Below we calculate the impact that these changes in the 'groundwater' and sediment may have on the arsenic concentration in the groundwater. These impacts are calculated sequentially and cumulatively in steps in order to show their separate impacts. In practice, they may not take place in the order given and probably will take place in parallel, at least to some extent. Calculations were made using PHREEQC (Parkhurst and Appelo, 1999) and ECOSAT (Keizer and van Riemsdijk, 1998). The calculations are meant to be demonstrative rather than definitive. Clearly others sets of assumptions would be equally valid.

Change in pH (Step 1)

There is likely to be a reduction in pH in going from river water to groundwater principally due to the increase in pCO_2. The median pH of Bangladesh groundwaters is close to pH 7 (Chapter 7, *Hydrogeochemistry of three Special Study Areas*). Therefore a pH change of one pH unit or more is possible, say from pH 8 to pH 7. In our simulations, the pH was adjusted by the addition of HCl since we did not want to simulate all proton reactions. Redox status was controlled by maintaining the partial pressure of oxygen at atmospheric levels.

In the presence of the baseline 0.03 mg L^{-1} dissolved P, the 'groundwater' As concentration actually increased by changing from 1 μg L^{-1} to 1.5 μg L^{-1} as the pH changed from pH 8 to pH 7. Phosphate was added to maintain the given dissolved P concentration. This change is the reverse of that expected in the absence of phosphate. This effect of P in reversing the pH dependence of As(V) sorption was noted earlier (Volume 4; DPHE/BGS/MML, 1999). This inversion in the pH dependence has not, to our knowledge, been demonstrated to take place in practice.

Competitive interactions: phosphate increase (Step 2)

Increasing the dissolved phosphate-P concentration to 1 mg L^{-1} at pH 7 by adding phosphate to the system increased the dissolved As concentration to 266 μg L^{-1} due to species competition and electrostatic effects. Adding even more phosphate would further increase the groundwater As concentration. This P concentration is not excep-

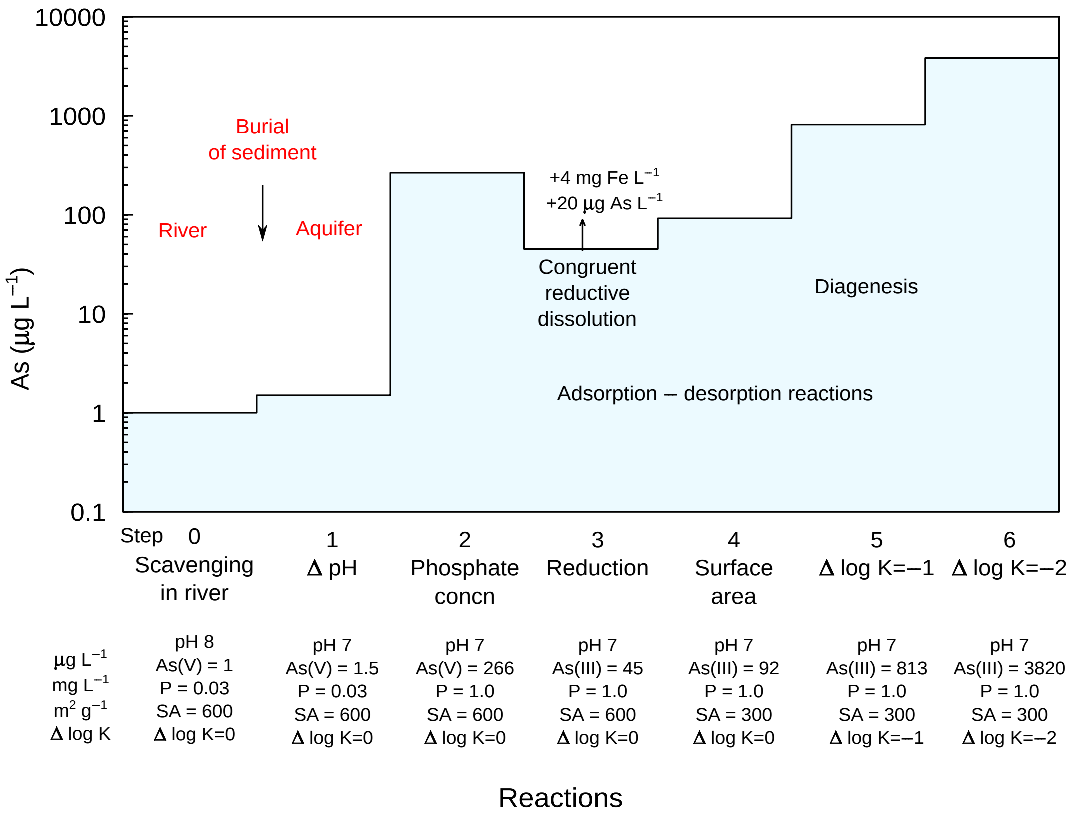

Figure 12.8. Change in the calculated arsenic concentration in groundwater as a result of changes in the amount of As adsorbed to iron oxides. The stepwise changes in groundwater chemistry or model parameters leading to this adsorption/desorption are indicated. The starting condition is river sediment with iron oxide in equilibrium with river water containing 1 µg L^{-1}. The changes are assumed to be sequential and cumulative from left to right. Δ log K is the change in the intrinsic As(III)-Hfo binding constant. All calculations are based on the Dzombak and Morel (1990) diffuse layer model and their default thermodynamic database for Hfo. The calculations indicate that the indicated adsorption/desorption reactions can 'magnify' the initial water concentration of 1 µg L^{-1} by more than three orders of magnitude.

tional for Bangladesh groundwaters. Weathering of phosphate minerals such as apatite, decomposition of organic matter, desorption of adsorbed P, fertilizers and even pollution could all increase P concentrations.

Redox changes (reduction) (Step 3)

Changing from oxidising to reducing conditions by reducing log pO_2 to –70 converts all of the As(V) to As(III). A constant total dissolved P concentration of 1 mg L^{-1} was maintained by adding phosphate to the system and a pH of 7 and ionic strength of 0.05 were maintained as before. The net effect of this redox change was to decrease the groundwater As concentration to 45 µg L^{-1}, a somewhat surprising result and again the reverse of the trend expected in the absence of phosphate. In other words, the presence of reductive desorption of As due to a change in arsenic speciation may depend on the phosphate concentration present. Phosphate is expected to be a better competitor for As(V) than As(III) (Figures 12.5 and 12.6). Again, whether this reflects reality remains to be seen. Anecdotal information suggests that the removal of As(III) by iron precipitation in Bangladesh groundwaters is less effective than might be 'expected' because of the presence of As(III) rather than As(V) which suggests that it might not be true (or is this simply a phosphate effect?).

Congruent dissolution (during Step 3)

Reductive dissolution of iron oxides is clearly an important process in Bangladesh aquifers. It produces high dissolved iron concentrations. Although the concept of congruent dissolution of solids with adsorbed species is not a straightforward one, it is informative to calculate the magnitude of As release that might be expected if it is assumed that the arsenic is uniformally distributed in the oxide phase and that the oxide dissolves congruently. We do this by assuming that the As/Fe mole ratio in the initial solid phase is preserved during dissolution.

Using the As and Fe data from the oxalate dissolution of Bangladesh sediments (Figure 11.17), we estimate that a sediment with 1% Fe_{ox} has an average As_{ox} of 4 mg kg^{-1}. In a 4 mg Fe L^{-1} groundwater, congruent dissolution would only be expected to release 1.6 µg L^{-1} As. This is a minimal contribution to the observed As load of contaminated groundwaters and is insufficient to account for the high As concentrations observed.

If the calculated As concentration in the Hfo just before the reduction step (3.3e-2 mol As kg^{-1} Hfo) is used, then the congruent release of As in the case of 4 mg L^{-1}

would be 16 μg L^{-1} As, an order of magnitude greater but still insufficient to account for the observed high As concentrations.

Reduction in specific surface area (Step 4)

The specific surface area of Hfo used in Steps 1–3 above was 600 m^2 g^{-1}. It is likely that with ageing, the Hfo will show a gradual reduction in specific surface area and an increase in particle size as a result of crystallisation to a more stable mineral structure. Haese et al. (1998) found a decrease in specific surface area of iron oxides below the redox boundary in pelagic sediments from the eastern and western equatorial Atlantic. This is a form of diagenesis. In our calculations, we assume that the surface site density (sites per nm^2) and binding constants remain unchanged.

As can be seen from Figure 12.8, Step 4, a decrease in the specific surface area to 300 m^2 g^{-1} has resulted in an increase in As concentration to 92 μg L^{-1}. Under these conditions (high P), the dissolved As concentration increases nearly linearly with decreasing surface area.

Reduction in binding affinity of the arsenite ion (Steps 5 and 6)

A second possible impact of diagenesis is a change in the bulk (mineral) and surface structure with a consequent change in the binding affinity for all adsorbed ions including arsenic species. This could reflect the formation of mixed Fe(II)-Fe(III) oxides including green rusts. As discussed in Table 12.1, this could lead to a reduction in binding affinity which would trigger an additional release of As. For example a reduction by one log K unit in the binding constant of As(III) (i.e. log K from 5.41 to 4.41) increases the calculated groundwater arsenic concentration to 813 μg L^{-1}. A reduction by two log K units gives a groundwater arsenic concentration of 3820 μg L^{-1}. Changes to the As(V) binding constant in these calculations are not relevant since all of the As is assumed to be As(III). However, if As(V) were present, then a similar reduction in the affinity of those binding constants would have a similar effect.

Conclusions from the model calculations

- Starting with a river sediment containing Fe(III) oxides and in equilibrium with river water containing 1 μg L^{-1} As(V), calculations show that it is possible to produce groundwaters containing hundreds or even thousands of μg L^{-1} of As by desorption processes.
- Many factors affect the scale of this 'magnification' in As concentrations including the chemistry of the river water and groundwater and the nature of the sediments in both the river and after burial in the aquifer.
- Competitive interactions at oxide surfaces (e.g. with phosphate) can lead to modelled reversals in pH and redox dependence, and to important changes in the calculated slopes of the As adsorption isotherms which tend to become more linear.
- It is the difference between the amount of sorption by the river sediment when initially buried and the present-day sediment that is important, not the absolute magnitudes of their sorption.
- An important factor could involve various diagenetic changes to the structure of the iron oxide minerals following burial. These could include a change in composition towards a mixed Fe(II)-Fe(III) oxide, a reduction in specific surface area and a change in binding affinity for As(V) and As(III).
- Therefore model calculations have demonstrated that, providing the correct conditions are met to promote As desorption, it is not necessary to invoke any form of exceptional 'arsenic contamination' in the original sediments in order to give groundwater As concentrations greatly exceeding the WHO drinking water guideline value – it can occur with 'average' sediments containing a few mg kg^{-1} of arsenic.
- The adsorption/desorption reactions can be described using the Dzombak and Morel diffuse layer model (DLM) but at present there are insufficient experimental data over the relevant range of conditions to be confident that the predictions are reliable. Furthermore, other minerals such as clays may also be important for adsorption and the DLM has not been tested adequately for these.
- The CD-MUSIC model of Hiemstra and van Riemsdijk is the most promising model for a quantitative description of these competitive interactions but the required model parameters need to be established for all of the important reactions.
- The calculations above have shown that adsorption/desorption reactions are very sensitive to may parameters including other basic water quality parameters. Since we know that the Bangladesh groundwater quality is highly variable, it is likely that the role of adsorption/desorption reactions will be similarly variable, and consequently particularly difficult to model accurately.
- Laboratory experiments need to be carried out urgently to quantify these sediment–water interactions in detail. This will lead to an improved understanding of the processes involved, better models and databases, and ultimately improved predictions. Such models are needed to inform water resource planners of the possible impacts and sustainability of the future use of deep and shallow tubewells in Bangladesh.

12.4.4 Reductive codissolution

We have demonstrated above that reductive (congruent) dissolution of As-rich iron oxides alone is insufficient to account for the development of the high-As groundwater concentrations observed. In principle, adsorption-desorption reactions probably could. In reality, dissolution and desorption reactions occur simultaneously in just the same way that during the precipitation of a new solid phase trace ions are incorporated into the phase, a process called coprecipitation.

Sometimes coprecipitation is indistinguishable from adsorption onto the evolving solid phase, as in the case of the coprecipitation of many divalent cations during the formation of Hfo (Kinniburgh and Jackson, 1981), i.e. it makes no difference whether the trace ions are added before the precipitation of the major mineral phase or afterwards. In contrast, coprecipitated ions are irreversibly incorporated into the bulk solid structure and become increasingly less accessible to exchange with the surrounding solution ions as diffusion and reaction proceeds. This leads to the formation of a solid solution. In this case, the sequence of mixing is important. This is likely to be true with anions such as phosphate, arsenate and arsenite.

The incorporation of impurities during coprecipitation can itself alter the mineral properties and affect the rate of 'ageing' or recrystallisation of the mineral, usually by slowing it down. For example, when arsenic was coprecipitated with Fe to form an As-containing Hfo, more As was incorporated than when a similar amount of As was added to a preformed Hfo precipitate because of the larger surface area (smaller particle size) of the coprecipitated Hfo sample (Waychunas et al., 1993). The presence of As 'poisons' the Hfo surface and slows down recrystallisation.

The science of coprecipitation is rather 'murky' but is of undoubted importance in the natural environment – it is probably the rule rather than the exception. Natural minerals contain a wide range of trace impurities. The reverse process, which we can call *codissolution*, is likely to be equally important. Where this dissolution is driven by reducing conditions we have *reductive codissolution*.

Therefore a more realistic model for the release of arsenic, phosphate and other anions in Bangladesh groundwaters might involve both reductive dissolution and desorption and will lead to the simultaneous release of Fe and other coprecipitated 'metals'. Desorption occurs through competitive and electrostatic interactions at the mineral surface. In the case of arsenic, changing from oxidising to reducing conditions may of itself lead to the desorption of arsenic as a result of a change in the interactions of arsenate and arsenite species and the reductive dissolution of As-containing minerals.

12.5 TRANSPORT OF ARSENIC

12.5.1 Simple 1-D model of flushing

There are too many uncertainties at present to make a reliable model of the transport of arsenic in Bangladesh aquifers but it is instructive to begin to think about it by making some simple calculations. We consider a 50 m column of aquifer sand divided into five 10-m thick layers, i.e. 0–10 m, 10–20 m, etc. All the sand material has been assumed to be derived from river sediment in equilibrium with 1 μg As L^{-1} in the same way that was assumed in the preceding calculations and then the pH dropped, the phosphate increased and the sediment reduced as before (Step 3, Figure 12.8). The sediment in the depth interval 20–30 m is assumed to contain five times as much iron oxide as the other layers and unlike the other layers is assumed to have undergone diagenesis to Step 5 (Figure 12.8). This gives an initial pore water concentration of 45 μg As L^{-1} from 0–20 m and 30–50 m, and 905 μg As L^{-1} from 20–30 m. This is one way of generating a high-As zone. It is important to remember that all of the sediments have evolved from initial contact with a 1 μg As L^{-1} river water, i.e. essentially 'uncontaminated' water.

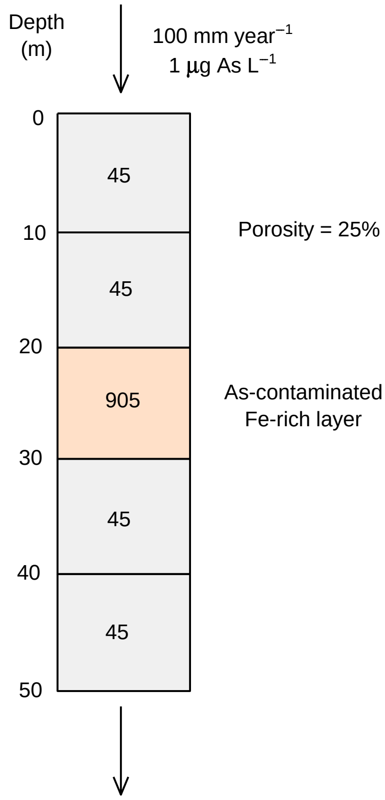

Figure 12.9. Five-layer model used to investigate vertical flushing of arsenic from a middle As-contaminated iron-rich layer of sediments (1% Fe compared with 0.2% Fe for the remainder). The numbers in the boxes are the initial dissolved As concentrations in μg As L^{-1}.

Fresh river-type water containing 1 μg As L^{-1} and 0.03 mg L^{-1} phosphate-P was then infiltrated from the surface at a rate of 100 mm a^{-1}. This rate is of the same order of magnitude as the rate of natural recharge (Chapter 5). If we assume a water-filled porosity of 25%, then this means that the water front will move at 400 mm a^{-1} (2.5 years per metre) or equivalently, it will take 25 years to cross one 10 m layer. (one pore volume) or 125 years to pass through the entire 50 m sand column. The configuration is shown in Figure 12.9. A uniform dispersivity of 0.5 m and a diffusion coefficient of 10^{-9} m^2 s were also assumed.

The results of 2000 years of flushing are shown in Figure 12.10. The highly-contaminated horizon decreases in concentration from 905 μg L^{-1} to 125 μg L^{-1} in the first 200 years. The curve represents the classic desorption front and its shape is related to the differential of the desorption isotherm (Appelo and Postma, 1994). The dimensionless partition coefficient for As is 130 in the less contaminated layers and 35 in the high groundwater As layer.

As a result of the downward movement of As from the highly contaminated layer, the layer beneath it increases in As concentration from 45 to about 180 μg L^{-1} after 140 years. The lowest layer at 40–50 m increases more slowly and does not reach its maximum arsenic concentration until after about 400–500 years. It also takes longer to flush the As away from this deepest layer such that even

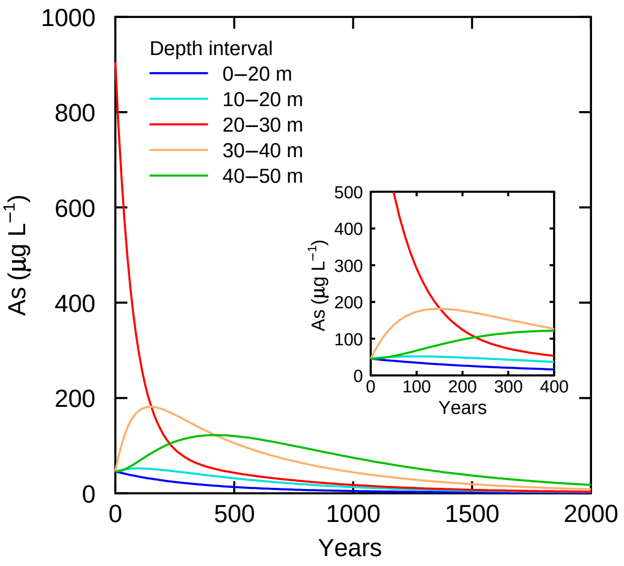

Figure 12.10. Simulated flushing of arsenic-rich groundwater from an Fe-rich layer at 20–30 m depth.The large groundwater arsenic concentration in that layer reflects the simulated effect of sediment diagenesis rather than an initially high level of sediment contamination. The inset shows a close-up of the early stages.

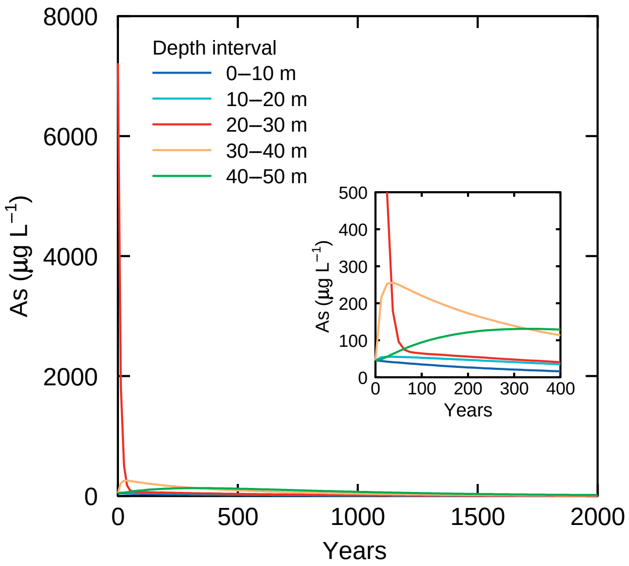

Figure 12.11. Simulated flushing of arsenic-rich groundwater from an Fe-rich layer at 20–30 m depth with very weak As(III) binding. Conditions are the same as in Figure 12.10 except that the As(III) binding constant has been reduced by an order of magnitude. The inset shows a close-up of the early stages.

after 2000 years and 160 pore volumes of 1 µg As L^{-1} water, the As concentration in this layer is still 17 µg As L^{-1}. By this time, the original heavily contaminated horizon has reduced to 3 µg As L^{-1}. The high-As horizon is high primarily because the As partition coefficient is low, not because it contained a lot of As. A corollary of this is that it is relatively easy to flush the arsenic from this horizon.

Arsenic is also slowly flushed from the top 20 m as the low-As 'river' water passes through these layers. The rate of reduction is slow and even after 1000 years, the As concentration in the top 10 m exceeds 10 µg L^{-1}. The arsenic from the top 10 m is leached to the 10–20 m layer and as a consequence, the As concentration in this layer reduces at an even slower rate.

Exactly the same simulation as above was then carried out with the only difference being that the affinity of arsenic(III) for the iron oxide in the contaminated horizon was decreased by a further factor of 10 (Δ log K=–2 from the original value). This could be because the oxide had undergone more diagenesis, for example. The dimensionless partition drops from 35 to 3.5 in the highly-contaminated layer. The total quantity of As in the system remains the same.

Reducing the strength of the arsenic binding induces a large desorption of As. This results in a corresponding greater initial peak As concentration of 7200 µg As L^{-1} in the contaminated layer (Figure 12.11). However, since this As is only very weakly bound, it is readily flushed out. After 75 years, the As concentration is below 70 µg As L^{-1}. It then remains close to that concentration for some time thereafter. The lower layer becomes the most contaminated layer as it receives the arsenic released from the higher layer.

These calculations highlight some of the features that can be expected to take place as arsenic is slowly leached from the Bangladesh sediments. In particular, it will be a period of slowly changing concentrations as the arsenic moves through the aquifer. The calculations highlight an important feature of the situation: are the variations in concentration due to changes in the total amount of As present or due to changes in binding affinity (or both)? Both can give rise to high concentrations of As in groundwater but their future evolution is quite different. The oxalate extracts suggest that variations in the amount of arsenic present are likely to be a factor.

While the above simulations are only indicative, i.e. they are completely dependent on the nature of the sorption isotherms assumed, they demonstrate several additional features: (i) during the natural flushing of the aquifer, some highly-contaminated areas will decrease in arsenic concentration while others will increase; (ii) the rate of change depends on the buffer capacity of the sediment and the distance from the contaminated region; (iii) the indicated timescales are long in human timescales, and (iv) the results are critically dependent on the adsorption isotherms and the rate of groundwater flow. These factors are themselves sensitive to many parameters and are subject to a great uncertainty at present. Therefore the timescales and concentrations observed above should not be taken to represent any particular situation in Bangladesh. Rather they should only be used to indicate the types of behaviour that might be expected, and perhaps more importantly, highlight what needs to be better understood before reliable predictions of arsenic transport in Bangladesh aquifers can be made.

More realistic simulations will also need to take into account the 3-D nature of the problem and include rivers and wells, as in a comprehensive hydrogeochemical contaminant transport model.

12.6 IS THE BENGAL BASIN GROUNDWATER ARSENIC PROBLEM UNIQUE?

As described above, the release of arsenic is a natural geochemical process that appears to be a response to the burial of 'typical' alluvial and deltaic sediments. Peaks of porewater As concentrations a few centimetres thick are often found in sediments. Indeed, the release of phosphate and to a lesser extent arsenic following the establishment of anaerobic conditions has been known since the 1970's. Where the rate of sedimentation is especially large, as in the Atlantic shelf region off the Amazon delta (Sullivan and Aller, 1996), the depth of this high arsenic zone can be up to a metre in thickness.

The large size of the Bengal Basin delta region and the recent history of very rapid sediment accumulation means that there is an unusually large volume and thickness of young, reduced sediments undergoing the early stages of diagenesis. This appears to be when the arsenic is released. Because of the unusual thickness of such recent sediments, the probability of drawing water from a highly contaminated zone is relatively high. In smaller deltas, the water from high-As zones (peaks) will tend to be diluted with water from low-As zones and the groundwater problem will be correspondingly smaller.

For the reasons given above, large delta regions probably do face an increased risk of having a significant groundwater arsenic problem compared with small delta regions. This is ironic since many of these large deltas are amongst the most densely-populated regions in the world and they usually have highly productive and readily exploitable aquifers. However, given the present state of knowledge, groundwater from all recent alluvial aquifers and deltas regions of the world must be considered 'at risk' from arsenic contamination and need to be screened for arsenic if they are to be used for drinking water.

Arsenic contamination of groundwater is also very extensive in other non-delta areas with recent sediments (e.g. the Argentine Pampas) but the population density in these area is usually much smaller than in delta regions.

12.7 SUMMARY

- The high correlation between arsenic and iron in Bangladesh sediments and the known strong sorption of As(V) and As(III) by iron(III) oxides suggests that these oxides play an important role in creating the high arsenic groundwaters in Bangladesh.
- Significant loadings of As(V) and As(III) occur on iron(III) oxides even at equilibrium concentrations of a few $\mu g\ L^{-1}$, a concentration which is probably characteristic of the concentration found in large rivers in Bangladesh. However, we could find no literature data for As concentrations in typical Bangladesh rivers.
- When sediment is buried, the oxidation of fresh organic matter rapidly leads to the development of anaerobic conditions and, we suspect, the release of arsenic.
- The precise mechanism of arsenic release is still unknown. It probably occurs by a variety of mechanisms including the reductive desorption of arsenic due to the transformation of As(V) to As(III), the reductive dissolution of iron oxides, and a change in surface structure and specific surface area of the iron oxides due to diagenetic reactions. We collectively describe all of these processes as the *iron oxide reduction hypothesis*. Arsenic release may also occur due to competition from other strongly bound anions such as phosphate, bicarbonate and silicate. Anything that causes an increase in the concentration of these anions is likely to lead to an additional desorption of arsenic.
- Desorption reactions rather than (congruent) dissolution reactions appear to be dominant although the two probably occur simultaneously in a process that can be called 'codissolution' - the reverse of coprecipitation.
- The As(V) and As(III) sorption isotherms for the oxidised (brown) and reduced (grey) sediments are not yet known and so it is not yet possible to calculate the arsenic transport properties of the sediments accurately. However, it appears that there must be a significant increase in arsenic mobility in the reduced sediments.
- The high solid solution ratio in aquifers means that immeasurably small changes in the amount of arsenic in the sediment can lead to a large change in the groundwater arsenic concentration. Total sediment arsenic concentrations are therefore not of themselves a reliable guide to the potential of a sediment to give a groundwater arsenic problem. This can occur with an average sediment containing only a few $mg\ kg^{-1}$ of arsenic.
- The low hydraulic gradients and the strongly stratified nature of the Bangladesh aquifers means that in the absence of pumping, the flushing of the released arsenic and other solutes is likely to be very slow. Although the calculations contain many uncertainties, this rate of flushing is unlikely to be helpful in improving the situation on a human timescale.
- Over many thousands of years, much of the arsenic will be flushed away and groundwater concentrations reduced. This may explain why high arsenic concentrations tend to be found mainly in relatively young sediments. Once equilibrium with the new groundwater environment has been achieved, there will be little need for the further release of arsenic.
- The generation of high arsenic groundwaters in Bangladesh is therefore believed to occur as a result of a natural geochemical processes that probably occur to some extent in all alluvial and deltaic sediments but are exacerbated in the Bay of Bengal because of the large volume of young sediments. All similarly exploited aquifers must be considered to be 'at risk' from arsenic contamination and, where they are exploited for drinking water, need to be tested for arsenic by random survey.