

13 Conclusions and Recommendations

13.1 PRINCIPAL FINDINGS

Below we summarise the main findings from our study. A more detailed account can be found in the Summary volume of this report.

13.1.1 Scale of the groundwater arsenic problem

A nationwide survey was undertaken to estimate the regional scale of the groundwater arsenic problem in Bangladesh. All arsenic analyses were carried out in the BGS laboratories using sensitive and reliable instruments. The results from the 3534 wells sampled throughout Bangladesh (apart from the Chittagong Hill Tracts) showed that 27% of all shallow wells (<150 m depth) were contaminated with arsenic (As) above the Bangladesh standard ($50 \mu\text{g L}^{-1}$). This increases to 46% when the more stringent WHO guideline value ($10 \mu\text{g L}^{-1}$) is used. 9% of all sampled wells exceeded $200 \mu\text{g L}^{-1}$ and 1.8% exceeded $500 \mu\text{g L}^{-1}$.

Only 1% of 'deep' wells (depth >150 m) exceeded the Bangladesh standard and 5% exceeded the WHO guideline value. This contrasts sharply with the statistics from the shallower aquifers. However, it must be remembered that most of the deep wells sampled were from only a small part of Bangladesh – the southern coastal region where salinity in the shallow wells is a problem, and from the Sylhet region in the north-east where there is no suitable aquifer at shallower depths. Recent data from DPHE tend to confirm this observation in other parts of Bangladesh but there is clearly a need for a more systematic study of the deep aquifer.

The population exposed to drinking water in excess of the Bangladesh arsenic standard was estimated in two slightly different ways: one estimate gave a population of about 35 million and the other gave an estimate of 28 million. These figures increase to some 57 and 46 million people, respectively, when the WHO guideline value is used. We have not been able to place reliable error estimates on these figures but believe that the larger of the two estimates is probably more representative. The total number of tubewells in Bangladesh is not known for certain but is believed to be in the range 6–11 million. The large majority of these are private wells.

A very large range of As concentrations is found in Bangladesh – from less than $0.25 \mu\text{g L}^{-1}$ to more than $2000 \mu\text{g L}^{-1}$. The severity of the problem varies over the country and is strongly related to geology. Only the young alluvial and deltaic Holocene sediments are affected – no contamination was found in the older Plio-Pleistocene aquifers of the Barind and Madhupur Tracts, and little in the alluvial fan deposits in the north and north-west. The most highly contaminated areas are found to the south and south-east of Bangladesh in an area centered around Chan-

dpur District. Some 90% of sampled wells in Chandpur District were contaminated according to the Bangladesh standard and practically all were greater than the WHO guideline value.

Seven deep wells from Dhaka city were sampled – these abstract their water from the old Dupi Tila aquifer of the Madhupur Tract and had very low As concentrations (all below the instrumental detection limit of $0.25 \mu\text{g L}^{-1}$).

8 of the 61 districts sampled had no samples exceeding the Bangladesh standard for As – these came from the extreme north-west of Bangladesh and from the southern coastal area where deep wells predominate. All districts except Thakurgaon had at least one sampled well exceeding the WHO guideline value for As.

13.1.2 Spatial variability of arsenic contamination

Within the overall trends dictated by the geology described above, there is very large amount of spatial variability. Much of this is very localised. Some 40% of the variation (in log terms) found over the whole country occurs within distances of about 2 km. Neighbouring wells within a village can have quite different concentrations of As (and other water quality parameters). This reflects the large amount of local variation in sediment characteristics and hydrogeological regimes, both laterally and vertically. A considerable amount of vertical variation in sediment characteristics is observed, often on a scale of centimetres, when undisturbed core material is examined in detail. The corresponding change in pore water chemistry is not known but could be similarly variable.

Dissolved arsenic concentrations vary with depth but not in a simple or predictable way. The two generalisations that seem to be valid are that very shallow wells (within say 5 m of the water table) tend to have quite low As concentrations and as discussed above, deep wells (greater than 150 m total depth) tend to have very low arsenic concentrations. It appears that there is therefore often something like a bell-shaped arsenic-depth curve with variable concentrations in the widely exploited intermediate depth range (around 15–150 m). These observations are derived from an analysis of wells at different locations but are consistent with our piezometer measurements where various depths were sampled at the same location (within a few metres). From our limited experience and that of others, hand-dug wells also invariably have low As concentrations even in highly contaminated areas. This probably reflects additional geochemical factors coming into play (see below).

As a consequence of the spatial variation, described above, all drinking water wells developed in the shallow Holocene aquifer (usually grey sands) must be considered 'at risk' from As contamination and need to be tested if they are to be used for drinking water.

13.1.3 Other water quality issues

Table 13.1 summarises the statistics for the exceedances of various inorganic parameters measured in this study. It is clear that arsenic is not the only groundwater problem, although it is undoubtedly the most serious. Manganese is also a serious problem in terms of the number and scale of exceedances. However, the chronic toxicity of Mn in drinking water at the concentrations observed is not well understood. The U.S. Environmental Protection Agency (USEPA) does not include Mn in its primary (health-related) drinking water standards although it does give it a limit of 0.05 mg L^{-1} in its secondary (aesthetic and cosmetic) standards.

Arsenic and manganese are not highly correlated and so there are some wells that fail on the arsenic criterion and some that fail on the manganese criterion. Only 33% of shallow wells complied with both the WHO guideline values for arsenic and manganese.

Uranium and to a lesser extent boron show some health-related exceedances as do some of the other trace elements. The USEPA has proposed a maximum contaminant level (MCL) of $20 \mu\text{g L}^{-1}$, equivalent to an activity of 30 pCi L^{-1} , for uranium in drinking water. This is ten times greater (less strict) than the provisional WHO guideline value.

Iron, ammonium and sodium (salinity) are present at undesirably high concentrations in many wells but are not thought to be a risk to human health. There are no data for mercury – this needs to be measured at a random selection of wells (taking appropriate precautions to avoid loss).

There needs to be a long-term policy decision for dealing with these other non-compliances. Lower than desirable concentrations of fluoride and iodide are found in some groundwaters, especially in the north of Bangladesh.

We have not looked for possible pesticide contamination. Pesticides are widely used in Bangladesh and a random reconnaissance survey of shallow wells should be undertaken to establish the potential scale of any problem. We have also not measured the concentration of radioactive elements such as radium.

13.1.4 Source of the arsenic

There is no doubt that the source of the As is natural, i.e. derived from 'ordinary' sediments by natural geochemical processes. The quantity of As present in groundwater (and adsorbed by the sediments) is simply too large to be derived from a discrete pollution source. Also its distribution across Bangladesh and West Bengal and with depth does not tally with a pollution source. There is also no need to postulate exceptional sources such as a particular mineralised area in the upstream catchment, as some workers have done for neighbouring West Bengal (Acharyya et al., 1999), although of course such areas may exist. This is one of the lessons that needs to be learned from the Bangladesh arsenic problem.

There is more than enough arsenic in most sediments to give rise to an As problem given the appropriate geochemical conditions for release and mobilisation. If all of the arsenic in a sediment containing 1 mg As kg^{-1} sediment dissolves in the groundwater, then the arsenic con-

centration in the groundwater would be $6000 \mu\text{g L}^{-1}$ or more, way above all drinking-water standards. Both the average world and typical Bangladesh sediments contain several times this amount of arsenic. In other words, Bangladesh sediments do not appear to contain an exceptional amount of arsenic *in total* yet give rise to exceptionally large groundwater arsenic concentrations. The high solid/solution ratio in aquifers and the great toxicity of arsenic mean that the contamination of groundwaters is sensitive to an imperceptible shift in the speciation of arsenic. A change of only a few per cent in the partitioning of arsenic between sediment and water is sufficient to give rise to a significant groundwater arsenic problem.

This is not to say that all sediments are equally likely to give rise to a groundwater As problem, or that Bangladesh sediments do not have some properties that make them particularly strong candidates for such problems. The greatest concentrations of As, along with many other elements, are associated with the fine-grained materials and these could therefore be a potential source of As. Fine-grained materials are found not only in fine-grained (non-aquifer) horizons, particularly clay horizons, but also to a lesser degree in the coarser, sandy horizons (aquifers). It may be that the concentration of fine-grained iron oxides in the coarse sediments is one of the important factors controlling the development of the groundwater As problem in Bangladesh and elsewhere.

There is also often a good correlation between the iron content of the sediment and its arsenic content. While iron is found in both iron oxides and iron sulphides, the low sulphur content of most Bangladesh sediments indicates that the dominant source of iron in these sediments is the oxides not sulphides. The structure of the iron oxides, the location of As on or within the oxides, and the binding strength for the surface-bound As are also important, i.e. the lability of the As.

It does appear, as a tentative generalisation from the small number of Bangladesh sediments studied in this project, that the higher the concentration of iron oxides in the sediments, the greater the likelihood of a groundwater As problem. This is consistent with the iron oxide reduction hypothesis in which the iron oxides are the principal source of released arsenic. This difference in iron oxide abundance appears to be an important reason for the greater prevalence of As in groundwaters from south-eastern Bangladesh compared with northern Bangladesh.

Somewhat confusingly, there is not necessarily a direct relationship between the As content of various sediments and the As concentrations in groundwaters in contact with such sediments – there may be other controlling factors. The mere presence of a good correlation between iron oxides and arsenic is also not by itself sufficient to indicate that the oxides are the dominant source of arsenic – the reverse could equally be argued, i.e. it could be that they are a sink. In practice, iron oxides buffer the arsenic concentration in the sediment pore waters and are both sources and sinks of As – they can both adsorb As and release it depending on the solution concentration and the surface loading with As as given by the sorption isotherm.

The concentration of iron in groundwater, and hence the extent of reductive dissolution, is also not necessarily directly related to the iron oxide content of the sediments.

Table 13.1. Exceedances of various inorganic chemicals observed in the DPHE/BGS National Hydrochemical Survey*

Parameter	Chemical symbol	WHO guideline maximum value (mg L ⁻¹)	Bangladesh standard (mg L ⁻¹)	% exceedance Shallow aquifer		% exceedance Deep aquifer		Comments
				WHO GV	Bangladesh standard	WHO GV	Bangladesh standard	
<i>Chemicals of health significance</i>								
Antimony	Sb	0.005 (P)	–	–	–	–	–	Not measured in NHS. SS data suggest not a problem
Arsenic	As	0.01 (P)	0.05	46	27	4.6	0.9	Serious problem
Barium	Ba	0.7	0.1?	0.2	28	1.2	26	Occasional problem according to WHO guideline
Beryllium	Be	NAD	–	–	–	–	–	Not measured in NHS. Rarely detected in SS (always <0.1 µg L ⁻¹)
Boron	B	0.5 (P)	1.0	2.8	0.4	29	8	Occasional problem especially in more saline waters
Cadmium	Cd	–	–	–	–	–	–	NHS data not sensitive enough. SS data showed no exceedances
Chromium	Cr	0.05 (P)	0.05	0.2	0.2	<1	<1	SS confirms essentially no problem
Copper	Cu	2 (P)	1	0	0	0	0	SS confirms no problem
Fluoride	F	1.5	1	–	–	–	–	SS and BWDB indicates if anything, too low especially in NW
Lead	Pb	0.01	0.05	–	–	–	–	NHS data not sensitive enough. Results from SS suggest not a problem
Manganese	Mn	0.5 (P)	0.1	39	79	2	22	Widespread exceedances sometimes of large magnitude
Molybdenum	Mo	0.07	–	–	–	–	–	NHS data not sensitive enough. Results from SS suggests not a problem
Mercury	Hg	0.001	–	–	–	–	–	Not measured
Nickel	Ni	0.02 (P)	0.1	6	0.1	0.9	0.3	Rare problem. Not exceeded in SS.
Nitrate	NO ₃	50	10	–	–	–	–	Not measured in NHS but SS indicates very low in most groundwaters. Greatest problem likely in shallow, polluted wells
Selenium	Se	0.01	0.01	–	–	–	–	Not measured in NHS but 20 samples were all <0.0005 mg L ⁻¹
Uranium	U	0.002 (P)	–	–	–	–	–	Not measured in NHS but results from SS suggest a significant exceedance especially in more oxidising waters
<i>Substances that may give rise to complaints by consumers</i>								
Aluminium	Al	0.2	0.2	1.7	1.7	6	6	Normally below 0.1 mg L ⁻¹
Ammonia	NH ₃	1.5	–	–	–	–	–	Frequent exceedances
Iron	Fe	0.3	0.3–1.0	68	55	32	15	Frequent exceedances
Potassium	K	10	12	10	8	4	2	Occasional problem especially in southern Bangladesh
Sodium	Na	200	200	8.5	8.5	49	49	Serious problem in coastal areas
Zinc	Zn	3	5	0	0	0.3	0.3	Not a serious problem

* See Chapter 6, *The National Hydrochemical Survey* and Volume 3, the *Hydrochemical atlas* for details.

– means no reliable data.

(P) – The Provisional guideline maximum value. This term is used for constituents for which there is some evidence of a potential hazard but where the available information on health effects is limited; or where an uncertainty factor greater than 1000 has been used in the derivation of the tolerable daily intake (TDI). Provisional guideline values are also recommended: (1) for substances for which the calculated guideline value would be below the practical quantification level, or below the level that can be achieved through practical treatment methods; or (2) where disinfection is likely to result in the guideline value being exceeded.

NAD – No adequate data to permit recommendation of a health-based guideline value.

NHS – DPHE/BGS National Hydrochemical Survey

SS – Detailed results from Special Study Areas survey (3 *upazilas*) carried out in this study (see Chapter 7, *Hydrogeochemistry of three Special Study Areas*).

Other factors such as the supply of reductants, the extent of microbial activity and the concentrations of other solutes are also important. The argument for oxides being a source term becomes stronger if diagenetic changes to the oxide structure are important since this provides a direct relationship between the amount of iron oxide in a sediment and the amount of arsenic released into the sediment pore water. These factors are not well understood.

It is not yet clear whether the arsenic presently abstracted in groundwater has moved from an area of fine-grained high-As sediments (which are not normally part of the screened interval) or whether it has been derived directly from the screened sandy horizons. Insufficient is known about the movement of As between the various horizons in Bangladesh aquifers to answer this point. We suspect that in some cases there has been movement, particularly close to the surface, but that this is not necessarily generally so. The fine-grained horizons will tend to be naturally protected from rapid leaching by their low permeability. Diffusion processes will be important over the longer term.

It is difficult to derive detailed mechanisms of geochemical processes from field data alone, especially from general survey data. There are simply too many correlated variables and the natural variability provides a blanket of 'noise' which obscures the underlying relationships. The processes involved need to be studied in detail both in the field and in the laboratory.

Furthermore, the natural process of chromatographic separation during groundwater flow means that the various products of geochemical reactions will become spatially separated with time. This 'uncorrelates' the chemistry and obscures the nature of the release mechanisms involved, thereby greatly complicating simple interpretations of groundwater-quality variations.

Once released from the sediment, the arsenic will be slowly flushed away ultimately emerging in a river (to be re-oxidised and re-adsorbed by the river sediments) or to emerge from the sea-bed in the Bay of Bengal. The extremely low relief in Bangladesh leads to very slow rates of groundwater movement, especially at depth which means that this flushing will take thousands of years to take place – this is not long on the geological timescale, many aquifers in the world consist of sediments that are millions of years old. Limited evidence from groundwater 'dating' techniques confirms the relatively old age of the deeper groundwater, especially in south-east Bangladesh, and hydrogeological calculations suggest that it could take several thousand years for the shallow aquifer to be flushed once. It will probably take many pore volumes of fresh water to pass through the aquifer before the As is completely flushed out – this depends on the nature of the As sorption isotherms which are presently largely unknown. The rate of flushing during the last glacial period would have been much faster than at present and may account in part for the very low As concentrations found in older sediments.

13.1.5 Changes with time

There are very few reliable data for the changes of As concentration with time. Changes can be expected at various

scales from hourly to decades and longer. Some of these can be expected to be fluctuating, others will show systematic trends reflecting the various geochemical and hydrogeological processes involved. The extent of these changes is expected to vary with location, including the depth of the well, and the depth to the water table and redox boundary and the location of highly contaminated zones. In general, the deeper the well, the smaller the likely variation with time. There is an urgent need for a long-term monitoring programme to be set up and maintained in Bangladesh. This should examine all the timescales of variation since they all have important implications – both for field testing and for long-term water resources planning;

This project installed sets of closely-spaced piezometers terminated at different depths in our three Special Study Areas. In these, water level and water quality were monitored every two weeks for up to one year. There was some variation in As concentrations, and other water quality parameters, but usually not that much and none that we could confidently say was a real reflection of changes in the aquifer with time. We experienced some difficulties in ensuring adequate quality control in sample collection and analysis. This monitoring should be continued with additional safeguards.

13.1.6 Broader consequences

The finding of high As concentrations in groundwaters from the Bengal Basin raises questions about the As concentration in groundwaters from other delta regions in the world. This is especially true if, as we believe, the contamination is entirely natural and does not require exceptional concentrations of As in the sediments. The scientific literature contains many references to enhanced pore water concentrations of As (and related P) from river, lake and ocean sediments. These are usually seen as small peaks in concentration a matter of a few centimetres or tens of centimetres below the water-sediment interface, and are usually associated with the onset of reducing conditions and iron oxide dissolution.

The geochemical processes therefore appear to be widespread but their scale is very variable. Historically, the rate of sedimentation in the Bay of Bengal is amongst the highest in the world, and the volume of young sediments is therefore correspondingly large (as is the degree of exploitation of the aquifers). Since it is in young sediments where the arsenic problems are greatest, the scale of the problem in Bangladesh is also likely to be exceptional in scale. All similar delta regions where groundwater is used for drinking water therefore need to be tested for As as a matter of some urgency.

13.2 GROUNDWATER TESTING FOR ARSENIC

13.2.1 The mitigation strategy

The scale of the arsenic problem in Bangladesh is clearly very large, as is now widely acknowledged. A detailed discussion of many of the issues involved is given in WaterAid (2000b). The fact that not all wells have yet been systematically tested should not delay rapid action to supply low-As water to all affected localities (Smith et al., 2000). Future

testing should be clearly focused on helping the mitigation effort, i.e. solving the problem, not documenting it.

The arsenic map of Bangladesh shows that there are clear regional differences in the extent of contamination and that these differences are dictated to a considerable extent by the underlying geology. The aquifers derived from older sediments of the Barind and Madhupur Tracts and deeper aquifers more generally do not appear to have a serious arsenic problem, at least at present. It is the aquifers derived from 'shallow' young, grey (reducing) sediments that give rise to most of the problematic groundwaters.

As a consequence of the high degree of short-range spatial variability in As concentrations, all wells in the 'at risk' aquifers identified above need to be tested for arsenic if they are used for drinking water. This is a mammoth task and presents severe technical, institutional and social challenges. The scale of such testing is likely to be feasible only by using field-test kits.

There are many possible approaches to arsenic mitigation and difficult decisions need to be made and acted upon. For example, there needs to be an acceptable balance between further testing and the provision of safe drinking water. It may be decided that in areas known to be highly contaminated, there is no need to test all wells immediately but that the resources would be better applied to the provision of safe drinking water for all as rapidly as possible. On the other hand, to ignore the presence of acceptable low-arsenic wells in a contaminated area might be counterproductive.

This testing is presently being coordinated by The Bangladesh Arsenic Mitigation Water Supply Programme (BAMWSP, www.bamwsp.org) with others, including DPHE, UNICEF, WHO and many NGO's, being actively involved (WaterAid, 2000b). Implementing a mitigation strategy involves many difficult decisions and is a massive task in terms of organisation. All strategies face some risk since there is no precedent for a response of the magnitude required. Sharing of non-contaminated wells is one emergency option. Locating all small, localised arsenic hot spots in northern Bangladesh also poses a problem (although not a high-priority one).

A top priority in any case must be to locate as many As-affected patients as rapidly as possible through mass awareness and screening campaigns. Once a patient is identified and a decision made about the best option for the provision of safe drinking water, then a follow-up testing programme around the patients' home could be carried out to indicate the scale of the local problem. Such a patient identification approach would not pick up some badly-affected areas, e.g. in the south-east, where there are few patients but considerable contamination. However, these areas have now been quite well identified and action should be taken there anyway.

Much depends on the willingness of the people to alter their way of life, probably in a way that will involve significantly more work, particularly for women. Tubewells are popular because they are convenient (in the absence of a distributed water supply). This situation is made all the more difficult by the complete absence of obvious, visible signs of arsenic poisoning in some of the highly contaminated areas. Often the water looks good and tastes good,

and nobody seems to be suffering, yet. There is therefore a credibility problem.

While the arsenic problem is likely to be the most serious in terms of its possible health impact, there are other causes of concern too, particularly of manganese which frequently exceeds both the Bangladesh drinking water standard and the WHO guideline value. The long-term mitigation effort must consider all possible threats not just that of arsenic. This could affect the relative merits of different arsenic mitigation strategies.

13.2.2 Field-test kits

The 1997 DPHE-UNICEF survey used field-test kits to provide the first nationwide view of the extent of arsenic contamination in Bangladesh. The recognised shortcomings in the reliability of the field test-kits used were offset to some extent by the large number of tests undertaken. The regional pattern was clear and has been largely confirmed by subsequent testing. This was a good use of these field-test kits. Compliance testing of individual wells is more demanding since breaching a national standard in a public water supply is particularly serious given the number of people affected (and the potential political fallout) while condemning a privately-owned well from use is also a serious step to take.

The reliability of the test kits for this type of testing is therefore of greater importance than in regional reconnaissance surveys. It is also significant that the arsenic concentration in water from many of the wells (not just a few) in Bangladesh lies close to the present Bangladesh standard. This means that if a two-way classification is used (fit and not fit) many wells will be 'misclassified' or their classification may genuinely change from day to day. This is not necessarily important from a health point of view but may lead to confusion when the public understanding of risk is so poor.

While doing anything is probably better than doing nothing, we think that a field-test kit specification with a detection limit of 5–10 $\mu\text{g L}^{-1}$ is highly desirable and in principle now possible. By 'reliable' we suggest that a determination should give results within $\pm 20\%$ of the true value or $\pm 5 \mu\text{g L}^{-1}$ (whichever is the greater), 95% of the time. Development of the kits should proceed in parallel with the overall mitigation effort and need not delay it. The kit should also be robust and simple to use so that it can withstand the rigours of continuous use in Bangladesh and elsewhere. Ideally the kits should be able to be manufactured in Bangladesh and sold in the local markets along with their chemicals. These would have to be of high purity. One-off and recurrent costs are also important. The kit should obviously work well in the region of 50 $\mu\text{g L}^{-1}$. The development and mass production of such a kit is an important technical challenge posed by the Bangladesh arsenic problem. WaterAid (2000b) lists all of the test kits presently available in Bangladesh. The latest generation of kits is looking much more promising. The better kits no longer give just a 'yes'/'no' response but are semi-quantitative.

Hach (USA) have recently introduced a field-test kit for arsenic with gradations at 0, 10, 30, 50, 70, 300, and 500 $\mu\text{g L}^{-1}$. A small modification allows testing down to

5 $\mu\text{g L}^{-1}$. This is a significant improvement on earlier kits but the kit requires 5 separate chemicals to be added and is quite slow. We believe that a cut-down version (3 chemicals) is also being developed. The Hach kit minimises exposure to toxic arsine gas and in the full kit, a reagent has been added to remove the interference of up to 5 mg L^{-1} H_2S . The cost of the kit is \$95 (October 2000) for 100 tests (US delivery) and \$75 for a 100 test replacement reagent set, i.e. about \$0.50–1.00 per test (a shallow tubewell costs something like \$100 to install). Many of the latest improvements are in design rather than in additional costly hardware, e.g. greater sensitivity by concentrating the arsine gas onto a smaller area of filter paper, greater precision by improving the stability of the gas flow and the reproducibility of the gas-filter paper interaction.

The arsine generator with the latest 'Arsenator' gives a coloured spot on a small disk of filter paper. This can be read by eye down to 5 $\mu\text{g L}^{-1}$. If the calculator-style reader (PeCo75) is used to read the 'colour', the minimum reported concentration is reduced to 1 $\mu\text{g L}^{-1}$. Larger concentrations are reported in 1 $\mu\text{g L}^{-1}$ increments. This small instrument, manufactured by Peter's Engineering, Graz, Austria (peters.engineering@styria.com) and currently having a price of about \$800, is likely to be more suitable for field testing than the larger Arsenator that we used in Mandari. This also is significant progress.

One advantage of the greater sensitivity and reliability of this new generation of kits is that the improved data would also inform planners of the likely impact of changing the Bangladesh standard to a lower value, the present WHO guideline value, for example. If Bangladesh ever decided to adopt such a new standard, retesting of already tested wells would then not need to be undertaken. It is also desirable that laboratory retesting is reduced to a minimum, i.e. only sufficient to maintain adequate QA.

13.2.3 Priorities for screening and mitigation

Approach to mitigation

The challenge of the arsenic mitigation programme should be to reduce the cumulative intake of arsenic by the population of Bangladesh as a whole as rapidly as possible. In the sense that people in the most contaminated areas will have the shortest latency period before symptoms develop and that solving their problems would be the most rapid way of reducing the total intake of arsenic by the population at large, they should be given the highest priority. Priority in the mitigation should therefore be given to the badly-affected areas identified in the south and east of Bangladesh. At a regional level, the resources for such a short-term programme should be allocated according to the severity of the problem, based for example on the percentage of wells in a district that are affected, or on the average arsenic concentration in the area, or on the probability that the water quality standard in the area will be exceeded.

Exactly how this is done must be left to the health and water-supply professionals but mass awareness must be a key part of any programme (as it is). While there is a danger of overreaction if the severity of the situation is communicated, equally there is a danger of complacency if it is

not. It is difficult to appreciate the dangers when the water is so clean and clear, when people around you are not obviously suffering and when the more tangible and immediate benefits of tubewell water are so great. We would stress three key messages: (i) warning of the danger – everyone should be aware of the first signs of arsenic poisoning and should know where to go for diagnosis and treatment. It should be stressed that the absence of visible symptoms does not mean that all is well, that sometimes the damage is internal and not visible, that it may take many years before symptoms do develop and that the damage once done may be irreversible; (ii) tubewell water can still be used for washing etc but not for drinking or cooking. There should be clear advice on how to obtain safe drinking water; (iii) the drilling of all new tubewells in the shallow aquifer throughout Bangladesh should cease, even of private wells. Individuals should be encouraged to save their money until a better long-term option can be recommended.

A blanket screening of all *upazilas* is likely to dilute the effort required in the worst-affected areas and so will delay helping the most needy. The regional patterns shown by our national survey and the large DPHE-UNICEF field-test kit survey are likely to be sufficiently robust to be used in setting the priority areas. A precise knowledge of the percentage contamination in individual unions or *upazilas* is not necessary in order to implement such a programme. The overall picture is already clear enough.

In the absence of any reliable information on the long-term changes in arsenic concentrations with time, the best assumption for planning purposes is that the present distribution of contaminated wells will not change appreciably in the short term (in a systematic sense). The priority should therefore be to cover the whole of Bangladesh once, starting with the worst-affected areas, before re-measuring wells as some have suggested. Such re-measurements are likely to confound the picture and lead to delays. Once the initial screening programme has been completed, and some decisions made about the long-term solutions, the necessity for re-measurement and more regular monitoring can be reassessed. The arsenic concentration in Bangladesh groundwaters varies by more than four orders of magnitude. This is far greater than any time trends are ever likely to be.

Short-term (emergency) programme

Smith et al. (2000) have discussed a mitigation strategy for Bangladesh in a clear and rational way. They suggested that:

- the arsenic problem should be declared a public health emergency to facilitate the rapid allocation of funding and the prompt expansion of interventions;
- all cases of arsenicosis should be identified;
- in affected areas, an immediate interim source of 'arsenic-free' water should be identified and the implementation of a long-term solution begun;
- patients' progress should be monitored and the continued use of the interim source of water ensured until the long-term source becomes available;

- care for patients should be provided, including vitamin supplementation, lotions for patients with keratoses and treatment of infections.

They also suggested four possible short-term responses:

- identify nearby safe tubewells;
- provide a water filter (e.g. a candle filter) for each household;
- provide chemicals to be used daily to remove arsenic from drinking water;
- use surface water treated by filtration and chlorination.

They also suggested that highly contaminated wells should be closed once an alternative temporary source has been identified. There is no point in even attempting to treat the most contaminated wells.

Smith et al. (2000) also stated strongly that delaying action in order to be thorough in research and long-term planning can be a mistake. Compared with many other public health issues like malaria, cholera and tuberculosis, the solution to the arsenic problem is relatively clear cut. The challenge is to replicate a strategy such as that outlined above over the whole of Bangladesh and in a timely manner.

It can also be argued that a random survey of a small number of wells in all mouzas should be undertaken in order to locate possible 'hot spots' in otherwise less contaminated areas. At present, many of the worst hot spots have now probably been located as a result of patient identification and follow-up screening but there must be others somewhat less highly contaminated that will need to be found eventually. However, this should not be allowed to detract from the rapid implementation of the mitigation programme in the highly contaminated regions of the south of Bangladesh which have already been clearly identified.

Long-term programme

Household treatment is not ideal as a long-term solution. It would therefore seem preferable if the long-term drinking water supply does not require arsenic removal. There are four possible sources of low-arsenic water in Bangladesh:

- rainwater;
- treated surface (river or pond) water;
- dug well water;
- deep tubewell water.

These options need to be evaluated thoroughly not just in terms of arsenic but in terms of all water quality parameters, including bacteriological quality. Socio-economic factors are also important of course. Not all options are available everywhere and so a single solution is unlikely.

13.3 USE OF DUG WELLS

Our data from a limited number of sites in western Bangladesh indicate that As concentrations in dug wells are usu-

ally low at around $10 \mu\text{g L}^{-1}$ or less, i.e. they normally comply with the WHO guideline value and invariably with the $50 \mu\text{g L}^{-1}$ Bangladesh standard.

Our data are mostly for filtered waters and therefore represent minimal values if particulate matter is present in the water. However, our data for two unfiltered dug well samples did not show a large increase above the filtered samples. Larger particles can be easily filtered out using traditional methods.

Since traditional, large-diameter dug wells in Bangladesh are normally open to the atmosphere and tap the shallowest parts of the aquifer, they are particularly vulnerable to contamination from bacteria and other surface-derived pollutants. Data from our Special Study Areas also indicate that dug well waters contain relatively high concentrations of uranium (up to $47 \mu\text{g L}^{-1}$ in Chapai Nawabganj). Iron concentrations are usually very low in dug well water; manganese concentrations are often low but not necessarily so.

In view of the possible sensitivity of water-quality parameters including arsenic, uranium and nitrogen species to redox status, it is possible that the specific method of dug well construction could significantly influence water quality, e.g. traditional brick-lined dug wells vs modern concrete-lined 'ring' wells. Subtle changes in the design might be able to give improved water quality by changing the aeration and sanitary protection.

If the benefits of low As water mean that dug wells are to be used as part of the mitigation programme, care needs to be taken that these are constructed to a high standard including the appropriate sanitary seals. A hand pump should be fitted. It may also be necessary to disinfect the water.

Certainly the concentration of arsenic in dug wells is likely to vary with time for all sorts of reasons – they are necessarily close to a fluctuating water table, for example. However, this should not detract from the overwhelming evidence to date from both Bangladesh and West Bengal that in arsenic-contaminated areas, the water from dug wells is normally of substantially better quality in terms of arsenic than water from adjacent shallow tubewells.

As far as we are aware, nobody has studied the effect of continuous abstraction of water from dug wells on the arsenic concentrations in the waters and this deserves study. In practice, the yield of water available from dug wells is quite limited. Hence dewatering is likely to be the factor limiting the productivity of dug wells.

Dug wells do offer a possible water-supply option particularly for those areas where the other options are limited. As far back as 1997 in Chapai Nawabganj, DPHE moved a hand pump tubewell a few metres from a highly contaminated tubewell (more than $2000 \mu\text{g L}^{-1}$) to an existing adjacent low-As dug well with immediate benefit to the users.

13.4 USE OF DEEP TUBEWELLS

Our data, and that of others, show that deep groundwaters usually have low concentrations of As (and other detrimental trace elements). The As concentrations are usually less than $1 \mu\text{g L}^{-1}$ and would therefore comply with all existing national standards and the WHO guideline value.

Deep tubewells may therefore form useful alternative safe water sources, where deep aquifers exist. Only 2% of the deep wells sampled in our national survey exceeded the WHO guideline value for manganese (0.5 mg L^{-1}) whereas 39% of shallow wells did. However, our deep well data were from the SW and SE coastal districts of Bangladesh (Barisal, Sylhet, Lakshmipur, Faridpur, Khulna, Satkhira, Bagerhat, Patuakhali, Pirojpur, Bhola and Barguna) and from parts of Sylhet and Faridpur.

More surveys need to be carried out in the deep aquifers to test whether this is a general characteristic. Also, modelling needs to be used to test the possible impacts of long- and medium-term seasonal drawdown of high-As groundwater from shallow levels following increased abstraction of deep groundwaters. A basic hydrogeological resource assessment needs to be undertaken to assess the long-term sustainability of the deep aquifer, i.e. over the next 50 years, by which time the population of Bangladesh is estimated to be 230 million. It is clear that if the deep aquifer is to be extensively exploited, an aquifer protection strategy needs to be devised and implemented. This should include its possible exploitation for both drinking water and irrigation water. Some form of licensing may need to be introduced.

Some of the exploratory deep boreholes recently drilled by DPHE have shown salinity at depth. These were found as far north as Manikganj and Munshiganj. Therefore not all deep groundwater may be of potable quality. There is also considerable concern that extensive exploitation of the deep groundwater in southern Bangladesh may induce greater saline intrusion in the southern coastal belt where fresh groundwater is at a premium.

13.5 IN-SITU ARSENIC REMOVAL

13.5.1 Principles

The subsurface removal of As has obvious attractions and has been successfully used elsewhere in the world. It is usually linked to some form of artificial recharge. Two approaches are possible for the in situ removal of As in high-permeability aquifers. Both rely on microbiological reactions:

Oxidation of the groundwaters in situ

This relies on the strong adsorption of As (especially As(V)) by iron(III) oxides that are formed when reduced, near-neutral sediments and groundwaters are oxidised. The oxidation can be brought about by the injection of air or an oxidising agent such as hydrogen peroxide. The reaction is mediated by microorganisms.

In the Vyredox approach (Hallberg and Martinelli, 1976) developed in Finland for the in situ removal of iron and manganese from groundwater, a ring of wells injects aerated water around a central supply well. The water has to be degassed before injection. The iron precipitates in the outer part of the aquifer furthest from the supply well and then the manganese precipitates closer to the supply well. Clogging of the aquifer is not normally a serious problem in the life-time of the plant. It takes an induction period before the system works efficiently.

A Vyredox-type system is quite sophisticated and in its normal design is unlikely to be appropriate for rural Bangladesh. However, there are simpler approaches involving gravity infiltration which may be adaptable to local conditions. Experiments of this nature have been carried out in West Bengal with some success (CGWB, 1999).

If a sulphide-rich horizon is oxidised, then there will be release of significant amounts of sulphate which in extreme cases could exceed water-quality standards. There will also be a release of arsenic but this will be partially reabsorbed by the precipitated iron oxides. Some acidity will also be released. This will react with dissolved bicarbonate, and free solid carbonates if present, and in most Bangladesh situations should not result in a large pH change.

This approach would need the input of large amounts of oxidants to effect a redox change as oxidation of both dissolved and particularly exchangeable and solid constituents (Fe^{2+}) is needed. Such systems have now been successfully modelled (Appelo et al., 1999).

Sulphate reduction

Precipitation of sulphides, particularly iron sulphides, will tend to coprecipitate As and other elements and thereby reduce groundwater As concentrations. The reaction is mediated by microorganisms and is the subject of ongoing research (J. Saunders, personal communication, 2000). In most of the high-As areas in Bangladesh where the method would be most useful, there is insufficient native sulphate present in the groundwater to work unamended.

Sulphate would therefore need to be added in dissolved form using some kind of bed infiltration or lagoon. CaSO_4 seems the best form of sulphate to add. This would lead to the generation of iron sulphides (eventually pyrite) in situ in a manner that is somewhat analogous to the natural reduction process that occurs after saline intrusion.

13.6 PASSIVE SEDIMENTATION

It is common in Bangladesh to allow the Fe in high-Fe waters to settle out overnight following air oxidation. This removes excessive Fe and will also incidentally remove some As, Mn and phosphate by adsorption and coprecipitation. The amount of As removed will depend on many factors such as the pH of the water and the amount of As present and its speciation as well as the amounts of Fe, phosphate, bicarbonate, silicate, calcium etc. in the water. The median concentration of Fe in As-contaminated ($>50 \text{ } \mu\text{g L}^{-1}$) groundwaters from the NHS was 4.1 mg L^{-1} . Time, and the efficiency with which the flocs are separated may also be important.

13.6.1 Short-term settling

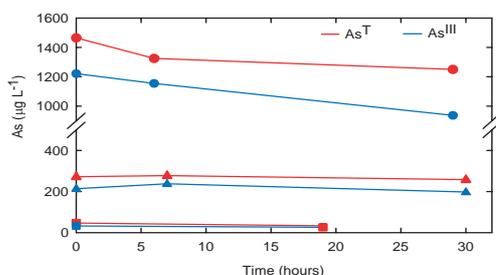
An analysis of Chapai Nawabganj groundwaters left to stand in the open air for periods of up to 30 hours was carried out in order to investigate the efficacy of the passive sedimentation approach. Samples were collected from boreholes at three sites: Rahaichar 1 and 2 and Goalpara. Groundwater from Rahaichar 2 was visibly cloudy (iron-oxide particles) on pumping but that from the other two

Table 13.2. Temporal variations in chemical composition of three water samples from Chapai Nawabganj after standing in a container open to air for various times

Time hours	As _T _{filt} µg L ⁻¹	As(III) _{filt} µg L ⁻¹	As _T _{unfilt} µg L ⁻¹	As(III) _{unfilt} µg L ⁻¹	As(III)/As _T %	pH	Fe _T _{filt} mg L ⁻¹	P _T _{filt} mg L ⁻¹
<i>Rahaichar 1</i>								
0	1460	1220	1380	1060	83	7.04	0.561	0.18
6	1320	1160	1420	1060	87		0.196	0.14
29	1250	937	1370	981	75	7.43	0.192	0.13
<i>Goalpara</i>								
0	272	214	279	199	78	7.16	0.757	0.32
7	277	238	285	184	86		0.049	0.18
30	258	198	269	184	77	7.53	0.167	0.15
<i>Rahaichar 2</i>								
0	46.5	32.2	126	<1	69	7.00	0.033	<0.1
19	33.0	26.0	78.1	40.7	79	7.44	0.024	<0.1

sites was clear. Samples from the sites had initial dissolved (filtered) As concentrations of 1465 µg L⁻¹, 47 µg L⁻¹ and 272 µg L⁻¹, respectively, with near neutral pH values (Table 13.2; Figure 13.1). Concentrations of As_T (unfiltered) were similar to the dissolved concentrations in the Rahaichar 1 and Goalpara samples, indicating that most of the As was present in dissolved form. However, the As concentration was more than 60% higher in the Rahaichar 2 sample, indicating that a significant amount of As was present in particulate form in this sample.

In all samples collected, As(III) constituted the dominant species (about 80% of total As) and remained so throughout the standing period. Oxidation of As(III) was therefore minimal over a period of a few hours. The pH was near neutral. During standing, the pH increased by about 0.4 units as a result of CO₂ degassing and oxidation of Fe(II) to Fe(III). Concentrations of dissolved Fe decreased during the experiments from 0.56 to 0.19 mg L⁻¹ in Rahaichar 1, from 0.76 to 0.17 mg L⁻¹ in the Goalpara water and from 0.03 to 0.02 mg L⁻¹ in Rahaichar 2. Concentrations of dissolved P were between 0.13–0.32 mg L⁻¹ in Rahaichar 1 and Goalpara but <0.1 mg L⁻¹ in Rahaichar 2 (Table 13.2).

**Figure 13.1.** Effect of time on the reduction in total dissolved arsenic and As(III) following passive oxidation of three tubewell waters from Chapai Nawabganj.

By the end of the standing period, total dissolved As concentrations had decreased slightly in all three samples, by between 5% and 30%. However, final concentrations in two cases remained above the Bangladesh standard and in all cases above the WHO guideline value. The lack of a substantial loss of As with time is believed to be due in part to the poor uptake of As(III) species and the relatively low concentrations of Fe. The increase in pH and the presence of a substantial amount of dissolved P will also tend to reduce the efficiency of any As(V) removal.

Phosphate tended to be reduced proportionately more than As (Table 13.2) because it was present as the strongly adsorbed phosphate species whereas As was present mostly as weakly adsorbed As(III) species.

13.6.2 Longer-term settling

We also took 28 unacidified but contaminated samples that had been collected during our surveys and reanalysed them for arsenic after several months of storage (and after re-filtering). This is a form of passive sedimentation with a long time allowed for oxidation. Iron oxidation is in any case rapid in unacidified samples, a matter of minutes or a few hours depending on the degree of aeration, and so the precipitation of Fe should be similar to that expected from a typical passive sedimentation experiment. However, as indicated above, As(III) oxidises more slowly and so this long-term experiment will contain a higher proportion of As(V) than a typical field experiment. In this respect, it should give maximal removal of As since As(V) is probably coprecipitated more efficiently than As(III) in Bangladesh groundwaters.

Even after standing, most of the waters exceeded the Bangladesh standard for As (Figure 13.2). As expected, the efficiency of As removal depended on the dissolved Fe concentration. Removal positively correlated with the Fe concentration before standing. Up to 80% of the As was removed when there was 10 mg L⁻¹ Fe in the water but less than 40% was removed when there was only 3 mg L⁻¹ Fe. However, while the iron removed some of the As, the As concentration remained above an acceptable concentration even in some of the waters with very high Fe con-

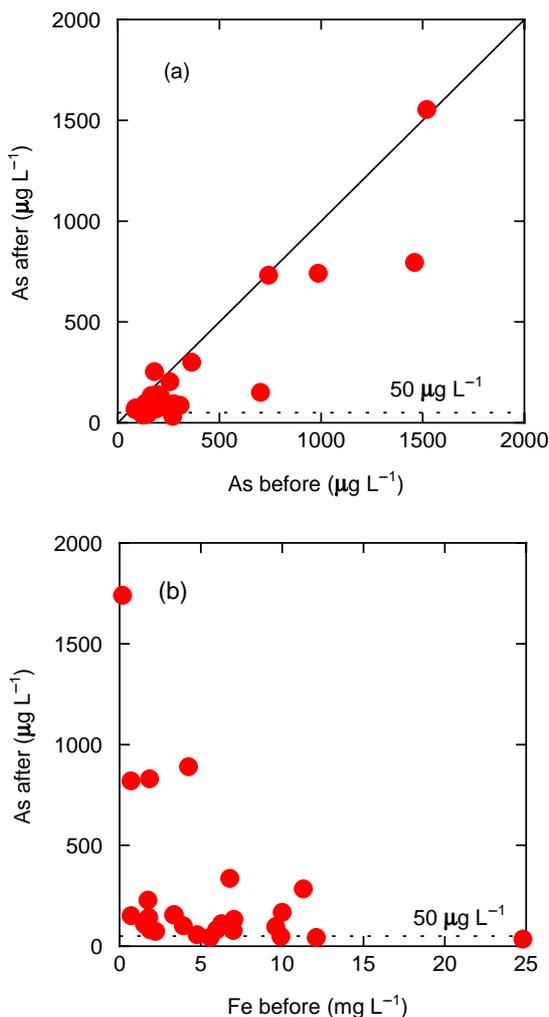


Figure 13.2. Comparison of As concentrations in a range of Bangladesh tubewell waters before and after a long period of standing. (a) change in As concentrations; (b) effect of initial Fe concentration on the final As concentration.

centrations (above 10 mg L^{-1}). In only four of the 28 contaminated waters did the treatment reduce the As to an acceptable level. This confirms the conclusion from field tests that while passive sedimentation may help in some cases, especially where there is high Fe, it is often not sufficient to bring contaminated waters to below the Bangladesh standard and is therefore not an ideal method.

There have been a number of other studies of the efficiency of passive sedimentation for removing As. For example, a recent test on 17 contaminated tubewells showed that passive sedimentation reduced the arsenic concentrations to below the $50 \mu\text{g L}^{-1}$ standard in just 2 of the 17 tubewell samples studied (WaterAid, 2000a). The As concentration in the remaining 15 samples was reduced to varying extents but not to below the standard. This agrees with model calculations and our ad hoc investigations of passive sedimentation.

It is of course possible to increase the efficiency of As removal by adding supplementary Fe or alum. An improvement in terms of As removal efficiency can also be

obtained by oxidising the As(III) to As(V). In the SORAS method (Gechter, 2000; Wegelin et al., 2000), this is achieved by adding a little lemon juice and exposing to sunlight. Arsenic removal efficiencies using the SORAS approach in Chapai Nawabganj averaged 67%. Adding a little potassium permanganate improves the removal efficiency still further.

The assumption that As mitigation can be significantly advanced by the widescale adoption of passive sedimentation (e.g. Nickson et al., 1998; 2000) is not accepted by most involved in the mitigation effort. While passive sedimentation will always reduce the arsenic concentration to some extent, Smith et al. (2000) caution against promoting this approach since it is not generally effective enough to reduce the cumulative dose and may delay the introduction of a more effective solution. Others involved in the arsenic mitigation effort in Bangladesh have adopted a similar line and it currently has 'no proponents' (WaterAid, 2000b).

13.7 SITING OF NEW WELLS

It is true that the more that is known about the detailed sedimentology, hydrogeology and history of an aquifer, the better any predictions about the extent of As contamination in the aquifer are likely to be. Bangladesh sediments show great vertical variability, often over scales of centimetres and this is unlikely to be predictable in a practical way. Detailed water quality surveys also often show great spatial variability over lateral distances of tens of metres. Reconciling these two aspects in many arsenic-affected villages would be an enormous (and expensive) task. Existing borehole logs also do not provide all the information required. It is a major undertaking to characterise the sediments geochemically, and while the relationship between sediment chemistry and groundwater quality will become clearer as more information is obtained, this relationship is at present far from straightforward. The sediment characteristics alone do not necessarily capture all the features of importance, e.g. the extent of past groundwater flushing, and because of the high solid/solution ratios in aquifers, water quality can be sensitive to imperceptibly small changes in sediment chemistry.

Very detailed studies, including laboratory studies, can be valuable for understanding the reasons for the observed variations in arsenic contamination in a few key places and therefore should improve our understanding of the processes involved, oxidation versus reduction, for example. Detailed field studies could lead to a better understanding of the problem that may lead to some useful 'rules of thumb' for well siting at a village level. Simply mapping the arsenic concentrations in existing wells will help to identify high-arsenic areas within a village. If a pattern emerges, this could be used to give some idea of the likelihood of finding 'uncontaminated' wells in an area. But as our experience in Mandari indicates, even this is likely to be difficult. Furthermore, given the scale of the problem already facing Bangladesh at present, it seems wise to minimise all further drilling of new boreholes in the shallow aquifer until the present situation is under control and can be reviewed objectively.

13.8 APPROACH ADOPTED IN THIS STUDY

The focus of this project was to understand the scale of the groundwater arsenic problem in Bangladesh and its causes.

We were aware from the outset that there was a paucity of data on many aspects of importance to the groundwater arsenic problem and we attempted to fill some of these more important gaps. The task has been made difficult by the complexity of the problem and the great degree of spatial variability found within Bangladesh. Statistics are very important and ultimately relate to risk. There is a great danger of being misled by the specific rather than seeing the general. We always wanted to obtain more data to establish the generalities with greater certainty. Even so, with more than 150,000 new pieces of data, much still remains uncertain about the detailed mechanisms of arsenic release.

We discuss below some areas of topical interest. Historians of science will no doubt review the lessons to be learned from the late recognition of the 'groundwater arsenic problem' in Bangladesh and elsewhere but we believe that the topic will lead to the exploration of new areas of science. Perhaps the greatest surprise has been the finding that sediments with 'average' arsenic concentrations can give rise to highly contaminated groundwaters under entirely natural conditions, a message that even today is not fully appreciated.

13.9 SOME AREAS OF CURRENT DEBATE

13.9.1 The nature of the debate

Much has been written recently about the Bangladesh groundwater arsenic problem in the popular press, on the web and in scientific journals. Some of this is enlightening but much is, in our opinion, ill-informed and poorly presented. While science thrives on open discussion and encourages dissenting views, this can provide a mixed message to policy makers and can cloud the real issues that deserve immediate attention.

Sometimes the differences appear to arise from the different use or interpretation of a word or phrase, as for example when discussing the population 'at risk' or 'deep tubewells'. Other times it arises from unwarranted attempts to generalise from the specific as in the discussion of arsenic release mechanisms or the arsenic-depth relationship. Sometimes it is based on ignorance of the situation in Bangladesh or of a basic misunderstanding of hydrogeology or geochemistry. Of course, sometimes the weight of evidence is insufficient to point to a single definite interpretation and so genuine differences are also perfectly reasonable.

Below we highlight what we consider are some of the important technical issues raised by the groundwater arsenic problem in Bangladesh and on which, in some cases at least, our project data provide useful new information. In a number of areas, our views differ significantly from those of others and so where appropriate, we provide the evidence that we have used to arrive at our conclusions.

Unravelling the detailed sequence of events that has led

to the development of highly-contaminated groundwaters in Bangladesh and elsewhere is a not a trivial task. It is a bit like forensic science: we can see the crime but have to establish a plausible explanation of how it happened, when it happened and the motives. As with forensic science, the best approach is first of all to painstakingly collect a wide variety of information (data), some of which may not at first appear to be directly relevant to the crime under investigation. Then all of this information is sifted through and the most plausible explanation that accounts for all of the then known 'facts' is sought. In difficult cases, lateral thinking helps. At first, there may be doubt in the assessment and we will have to adopt a 'balance of probability' approach. However, unlike investigating a real crime, we can be confident that given enough time and effort, science will eventually narrow down the possibilities to near certainty.

As yet, we are far from that position of 'near certainty' and so we readily admit that in many areas, the best that can be done is to speculate on the possible 'timing' and 'motives' of the groundwater arsenic problem in Bangladesh. Some of the statements expressed below have been attributed to specific sources; others are more general points of discussion that we have heard and believe deserve some response.

13.9.2 The number of tubewells in Bangladesh

There is no definitive estimate of the number of tubewells in Bangladesh. The uncertainty affects both the scale and planning of any comprehensive arsenic testing programme and the consequent mitigation effort required. It is less critical to estimates of the exposed population (see below) since most (97%) of the rural population is believed to use groundwater. The issue of the number of tubewells is therefore more concerned with the degree of sharing.

While the number of Government (DPHE)-drilled wells is about 1.2 million, there is no requirement for private wells to be licensed and so the number of these is far less certain. The results of the BAMWSP (NESP) survey of six *upazilas* (Chapter 6) found that there were just over six times as many non-Government wells as Government wells. Estimates of the number of wells has steadily increased since 1997. At present, the best estimate is probably in the range 6-11 million wells.

As more surveys are undertaken, these estimates should improve. The most reliable estimates are likely to come from comprehensive ('all wells') surveys such as the detailed village and *upazila* surveys undertaken by BAMWSP, NIPSOM, UNICEF and various NGO's. What is clear is that a large number of private wells have been installed in recent years, especially in the last decade. We found that 68% of the sampled wells in our National Hydrochemical Survey (n=3534) had been installed since the beginning of 1990. In our village survey in Mandari, the figure was even higher (86%).

Not all wells drilled remain in working order and so some distinction needs to be made between the number of wells and the number of operational wells. The recent NESP survey of six *upazilas* found that about 5% of the wells were not working. There was however considerable variation between the *upazilas*.

13.9.3 Reporting of the scale of the groundwater arsenic problem in Bangladesh

The following two statements were downloaded from the web and illustrate the confusion that can arise when words are used casually and without definition:

'The latest statistics available on the arsenic contamination in groundwater indicates that 59 districts around 85% of the total area of Bangladesh and about 75 million people are at risk. It is estimated that at least 1.2 million people are exposed to Arsenic poisoning with 24 of millions potentially exposed.'

www.dainichi-consul.co.jp/english/arsen.htm
(Dated March 25, 1999; downloaded 17 July, 2000)

'According to a survey, jointly carried out by Dhaka Community Hospital and School of Environmental Studies (SOES) of Jadavpur University, Calcutta in 1997, an estimated 75 million people are at risk of drinking arsenic-contaminated water and of developing its adverse effects.'

www.dainichi-consul.co.jp/english/arsenic/as82.txt
(Dated August 17, 1998; downloaded 17 July, 2000)

What do 'at risk', 'exposed' and 'potentially exposed' mean? What are the definitions of an 'at risk' district and 'at risk' people? What is the definition of 'arsenic-contaminated'? In the first statement, the 75 million people said to be 'at risk' does not seem to imply that they are all actually drinking arsenic-contaminated water whereas in the second statement, it does.

We think that it is useful to define terms as follows: an 'at risk' aquifer is an aquifer which shows sufficient indications of a possible groundwater arsenic problem to warrant the widespread testing of wells within the area in which that aquifer is exploited; an *at risk individual* is an individual drinking groundwater from an *at risk* aquifer, and an *exposed individual* is a person drinking above the prescribed limit for arsenic in drinking water. The *affected population* is the number of people with confirmed arsenic-related symptoms. Therefore not all 'at risk' individuals will be *exposed*. The number of exposed individuals will depend on the level of exposure used, i.e. the prescribed limit. In the context of Bangladesh this is typically either taken as $50 \mu\text{g L}^{-1}$ (the Bangladesh standard) or $10 \mu\text{g L}^{-1}$ (the WHO guideline value).

Risk varies on a continuous scale and so always needs careful definition. Some people use it in a quantitative sense while others use it only qualitatively. The definition of the number of people *at risk* given above is only qualitative and is highly dependent on the nature of the 'sufficient indications' - as the processes governing the formation of arsenic-affected groundwaters are better understood and as more data for a particular aquifer are obtained, the nature of the risk in a given area will be able to be refined. It may then be possible to exclude some areas from the *at risk* area. Eventually, as more and more testing takes place and the nature of the contamination becomes better understood, the *at risk* population should converge down to the actually *exposed* population. With these definitions, estimates of *at risk* populations must be treated with a great deal of caution since they attempt to quantify what is essentially a qualitative concept. We believe that estimates of the *exposed* population in a given area are of greater value

but are more difficult to calculate. We see no value in the term *potentially exposed*.

An analogy may help. Smoking is a well-known risk factor for lung cancer but not everybody who smokes will die of lung cancer. Living in an arsenic-affected district is a risk factor but not all wells in a district are necessarily affected and so not everybody in the area will be exposed to arsenic contamination.

Estimating the population currently exposed to 'arsenic-contaminated water' is difficult and there are many ways of doing it. Each way will give a different answer. For example, it obviously depends on the definition of 'arsenic-contaminated' used (e.g. $50 \mu\text{g L}^{-1}$ or $10 \mu\text{g L}^{-1}$) and in cases where only some of the wells have been sampled, both on the way in which the arsenic concentrations in the unsampled wells are estimated and the way that the number of people drinking from those wells are estimated.

Perhaps more relevant to an assessment of the health risk would be an estimate of the daily *dose* of arsenic from drinking water as a function of the population taking in that daily dose, that is, a dose density function. This would take into account the amount of drinking water actually ingested (hot countries such as tropical Bangladesh are known to have significantly higher intakes than temperate countries) and the fact that individuals may drink water from more than one well. If several wells are used per individual, then the approximately log-normal distribution of arsenic contamination means that highly contaminated wells will have a disproportionate influence on the number of people taking in an excessive dose of As.

Where every well in a village or *upazila* has been sampled, no extrapolation to unsampled wells is required for that area and the only sources of uncertainty arise from the estimates of arsenic concentration (contaminated or not) and the number of people drinking from a particular well.

However since most of the wells in Bangladesh have not yet been tested for arsenic, estimates of the arsenic concentration in the unsampled wells and the number of people drinking from these wells are necessary. This is essentially a statistical exercise and different *estimates* can be made depending on the data available and the assumptions made. Even with the same raw data, different scientists are likely to make different estimates. Hopefully though, these differences will be small.

At present, our National Hydrochemical Survey database probably provides the most readily available dataset for estimating the nationwide statistics for arsenic-exposed populations in Bangladesh. No other survey to date has combined both a uniform (and near random) national coverage with reliable (laboratory) analyses for arsenic at the $\mu\text{g L}^{-1}$ level, accurate recording of the location of wells (by GPS) and open reporting. The mere hint of any bias in the selection of wells is enough to throw the resulting 'statistics' into doubt. There are so many affected wells in Bangladesh that it would be easy to find a large number of contaminated wells either by using patient identification as a 'lead' or by adapting the sampling scheme to track down arsenic-rich areas as they are identified. This is one approach adopted by DPHE and others in their mitigation programme.

Randomisation of itself does not guarantee 'accurate' statistics since all estimates are themselves subject to an

uncertainty depending on the sampling and analytical uncertainty, the sample density and the nature of the spatial variability. The high degree of variability observed in groundwater arsenic concentrations in Bangladesh (more than four orders of magnitude) and the weak spatial dependence mean that a large number of samples will be required to establish reliable statistics. For example, with about 8 samples per *upazila*, our *upazila*-based statistics are subject to a large and perhaps unacceptable error while the district-based statistics based on about 50 samples should be more reliable and more acceptable. Of course, as the size of the area concerned is increased, the resolution and perhaps the usefulness of the results decreases.

The main assumption that we have made in estimating the exposed population is that the wells sampled in our National Survey were ‘randomly’ selected and so provided unbiased estimates of the distribution of arsenic contamination over the sampled area. While we accept that our site selection was not random in the strict sense, there was no intentional bias (in terms of water quality) and as yet we have no reason to suspect any such bias. Nevertheless we accept that our statistics should only be used as a guide and should be updated as more and better information becomes available. We wholly endorse the importance of the random selection of wells as the ideal in reconnaissance surveys but are aware of various practical problems preventing this from being always realised.

We made two estimates of the number of people presently exposed to arsenic concentrations exceeding the $50 \mu\text{g L}^{-1}$ limit in drinking water in Bangladesh based on different methods of extrapolating from sampled wells to the large number of unsampled wells. Method 1 used a technique called disjunctive kriging to estimate the probability of obtaining an arsenic-contaminated well in a given 5 km grid square while Method 2, which was based on discretisation over a whole *upazila*, used the percentage of contaminated wells in that *upazila* to estimate this probability. These probabilities were then multiplied by the estimated 1999 populations of people drinking water in the grid square or *upazila* and summed to give the exposed populations. This involved additional assumptions about the population of a grid square (same density as in the *upazila* as a whole or a weighted average where more than one *upazila* was involved), the population growth rate since the 1991 Census (2.1% per annum) and the percentage of people using groundwater for drinking water (97%).

Method 1 gave an estimate of the exposed population of 35 million people while Method 2 gave an estimate of 28 million. If a standard of $10 \mu\text{g L}^{-1}$ is assumed, these figures increase to 57 million and 46 million people, respectively.

We accept of course that these estimates are themselves both subject to error, and we are not sure how large these errors are. Errors arise both from the interpolation of arsenic concentrations and population density. Others, particularly Dhaka Community Hospital (see opening statements), claim that the number ‘at risk’ is closer to 75 million people. While we have not seen the detailed assumptions on which this figure has been based, we believe that it must assume that when a district has more than a certain number of contaminated wells, all people in that district are counted as ‘at risk’ to arsenic-contaminated

water. They are indeed ‘at risk’ in the sense that the probability that they are drinking contaminated groundwater may be quite high because they live in a generally arsenic-contaminated area but this is different from saying that they are all definitely ‘exposed’ to arsenic-contaminated groundwater. Our exposed population estimate includes an additional factor that accounts for the probability that a given well is contaminated (this varies from 0–1). Therefore care has to be taken to explain precisely what is being discussed in order to avoid confusion. If scientists cannot write clearly on these issues then there is little chance that the popular press will do so.

Finally, a statement such as ‘every round of water quality tests shows more wells exceed the Bangladesh standard of 50 parts per billion (ppb) for arsenic in drinking water’ is either stating the obvious or is ambiguous and therefore confusing!

13.9.4 Identifying the dominant mechanisms of arsenic release – oxidation or reduction?

The arguments about whether the arsenic problem in the Bengal Basin results from the oxidation of sulphide minerals or from reducing conditions have continued for some time. Case studies in other parts of the world have demonstrated that arsenic can be released by both mechanisms. The oxidation reaction has been much more widely studied and is better understood, mainly because it is the dominant reaction taking place in many mining areas, sometimes on a dramatic scale. It also involves readily-identified minerals.

We suspect that both oxidation of sulphide and reduction of sulphate are presently taking place in different parts of the Bangladesh aquifers, for example at different depths, at different times and in different places. There are demonstrable large differences in redox conditions, water levels, water-level fluctuations and sediment characteristics throughout Bangladesh and so demonstrating one particular mechanism at a particular location is not the same as demonstrating that it is the principal process taking place elsewhere. Isolated observations should not be allowed to confuse the discussion. It is the process that is dominantly associated with arsenic release into solution in Bangladesh aquifers that is of primary concern here, e.g. in the badly affected areas of south-east Bangladesh and in the hot spots of northern Bangladesh. We believe this to be normally associated with strongly reducing groundwater conditions and we have not seen any data suggesting the contrary. Amazingly, no data have ever been presented to support the pyrite oxidation hypothesis in Bangladesh.

It is sometimes said that the exact mechanism of arsenic release is of academic interest and not relevant to the mitigation effort. This is largely true for the emergency mitigation programme but not for the longer-term programme where some insight into the possible future impacts and interactions resulting from proposed policies is required. One hypothesis (reduction) implies that the processes are essentially natural and have been occurring for long periods of time, the other places strong blame on the recent ‘over-abstraction’ of groundwater as the cause of the As problem (‘over-abstraction’ is often used incorrectly in the Bangladesh context since while abstraction of irrigation water has increased the annual water table fluctu-

ations, full aquifer recovery normally occurs during the rainy season and there is no long-term decline in water tables). Continued 'over-abstraction' also implies that there will be a potential worsening of arsenic contamination with time. At the present time, this is only speculation.

The release mechanism therefore has important implications for future groundwater management, agricultural policy and ultimately rural livelihoods. It is therefore far from being only of academic interest and needs careful examination. A detailed understanding of the processes will also help scientists to identify other aquifers in the world most at risk.

13.9.5 Popular misconceptions relating to the source of arsenic

Pyrite is present and so must be the source of arsenic

Authigenic pyrite, although not abundant, has been observed in Bangladesh sediments from both shallow and deeper sediments (see Chapter 11). This has been used as evidence by some for the pyrite oxidation hypothesis. However, the presence of sulphide minerals in the aquifers proves neither the oxidation nor the reduction hypothesis. Pyrite is an expected end product of sulphate reduction, and its presence in the solid phase can therefore be used equally as evidence for sulphate reduction. Precipitation of iron sulphides will tend to scavenge some arsenic from the groundwater and will lower the arsenic concentration. Furthermore, where the sediments have been subjected to a marine influence either at the time of deposition or subsequently, relatively high sulphur contents in the sediments can be expected since seawater contains some 2700 mg L⁻¹ of sulphate. SEM photographs of Bangladesh sediments show euhedral pyrite grains not having been strongly weathered, which suggests that they are newly formed and points against active oxidation.

Although some scientists still propose that the oxidation of arsenopyrite is an important process in Bangladesh sediments, this is not supported by data and we know of no studies that have identified arsenopyrite as a common mineral in Bangladesh sediments. If anything, the culprit is pyrite, or some other iron sulphide mineral, which contains As as a minor constituent. But again we stress: no convincing evidence has yet been put forward to support this hypothesis.

Some sulfate minerals are very insoluble and would support very low levels of sulfate in solution. One such mineral, which is very prevalent in acid sulfate soils, is jarosite.'

(email discussion, D. Fanning, July 2000)

There is no observed positive correlation between As and SO₄ in either the National Survey groundwaters or groundwaters from the Special Study Areas. The spatial distributions of As and SO₄ are also very different. Arsenic and SO₄ concentrations should be positively correlated to some extent if sulphide oxidation is the main As-release mechanism. Indeed, the inverse relationship is observed in shallow groundwaters from the Special Study Areas and provides strong evidence that sulphate reduction accompanies As release. Relatively high SO₄ concentrations and more oxidising conditions are found in groundwaters from

some parts of northern Bangladesh (e.g. the Tista Fan). However, these have the lowest As concentrations. High As concentrations are found in the south-east of Bangladesh where SO₄ concentrations are generally low (<1 mg L⁻¹). Sulphate can also be derived from pollution sources but is usually accompanied by other pollution indicators such as chloride.

Sulphide oxidation must lead to SO₄ release and a consequent substantial increase in the dissolved SO₄ concentration. Shallow piezometers (10 m) and dug wells from Chapai Nawabganj provide samples from the zone of water-table fluctuation and close to the redox boundary. These do sometimes show significant increases in SO₄ relative to deeper groundwaters locally and are therefore candidates for possible sulphide oxidation. Nonetheless, As concentrations are notably lower in these groundwaters than at deeper levels. Where pyrite oxidation occurs and is accompanied by the oxidation of iron, precipitation of iron(III) oxides will usually occur with some resorption of arsenic. Some calculations (C.A.J. Appelo, personal communication, July 2000) suggest that as much as 90% of the released arsenic could be resorbed by these freshly precipitated oxides. In that sense, pyrite oxidation is a relatively inefficient mechanism for arsenic release.

In any case, there is no evidence to link iron sulphide oxidation with the generation of the high As groundwaters generally observed in Bangladesh. Therefore while iron sulphide oxidation certainly could be a mechanism for arsenic release, and should be seriously considered, we believe that it is as yet unsupported by hard evidence. Indeed, the reverse appears to be the case.

The lack of high sulphate concentrations in arsenic-affected Bangladesh groundwaters provides key evidence against the pyrite oxidation hypothesis. It has been proposed by some that pyrite oxidation is the primary mechanism of arsenic release but that some sulphate-containing mineral is forming that prevents the build-up of high sulphate concentrations in Bangladesh groundwaters. Several minerals have been suggested as possibilities: gypsum (CaSO₄·2H₂O), jarosite (KFe₃(SO₄)₂(OH)₆), and K-alunite (KAl₃(SO₄)₂(OH)₆). Saturation indices for these minerals in Bangladesh groundwaters are typically strongly negative and so their formation is highly unlikely. Qualitatively, gypsum is rather soluble and is normally only formed where sulphate concentrations are a few thousand mg L⁻¹; K-alunite is unlikely because of the near-neutral pH values and corresponding low Al activities, and jarosite is unlikely because it contains iron as Fe³⁺ not Fe²⁺ which is the dominant iron species in Bangladesh groundwaters. The mineral rozenite (FeSO₄·4H₂O) was observed in a Bangladesh sediment by Chowdhury et al. (1999). This mineral is typical of acid sulphate environments and was probably formed by oxidation after sampling, i.e. it is probably an artefact created during storage. The high-arsenic groundwaters of Bangladesh do not have the characteristics of acid mine drainage!

Therefore while there are occasional reports of these rare minerals in Bangladesh sediments, these are likely to be based on observations of partially-oxidised sediments since few workers have taken the very considerable efforts required to prevent oxidation following sampling. Many new minerals can form when Bangladesh's reduced sedi-

ments are allowed to oxidise. If claims for rare minerals known to be formed as a result of oxidation are identified and claimed to be present in Bangladesh aquifers, it is incumbent on the observers to provide a convincing case that this formation has not happened post-sampling.

Pyrite oxidation produces acid waters and since these are not generally found, this supports the reduction hypothesis

This is not a useful argument because of the widespread occurrence of solid carbonate minerals in Bangladesh sediments and the strong likelihood that these carbonates buffer the groundwaters at near-neutral pH values. The pH will then depend strongly on the partial pressure of CO₂. This in turn is governed by production of CO₂ from bacteriological oxidation of organic matter, dissolution of carbonates, and the diffusion of gaseous CO₂ to and from the atmosphere.

13.9.6 Evidence supporting the iron oxide reduction hypothesis

The release of small amounts of arsenic from recently-buried sediments appears to be a very general phenomenon that has been observed in river, lake and ocean sediments as well as in flooded soils (Smedley and Kinniburgh, 2001). Most young sediments are strongly reducing below a very thin oxidised layer. The study by Sullivan and Aller (1996) is indicative of the potential generality of the processes involved. They measured detailed pore water (dissolved) As and Fe profiles in sediments from the Amazon shelf region of the Atlantic ocean several hundred kilometres off the coast of Brazil. Even in this pristine and randomly selected environment, there was evidence of a broad pore water arsenic peak some 50–200 cm below the ocean-sediment interface. Peak As concentrations ranged up to 300 µg L⁻¹ with an average of about 135 µg L⁻¹. There was also a closely-related peak of dissolved Fe(II) concentrations, often peaking at a slightly shallower depth and several hundred times greater in magnitude (on a molar scale). Similar profiles have been observed in other studies of ocean sediments albeit at a much reduced scale.

It is easy to see some similarity between these results and our piezometer profiles albeit with the vertical scale stretched by an order of magnitude or more in our profiles. Many of the underlying processes that have been active in the Atlantic sediments are almost certainly similar to those that have been active in Bangladesh sediments and in reducing aquifers in alluvial and deltaic environments in other parts of the world (Chapter 2). Interestingly, Sullivan and Aller (1996) also found the same bell-shaped As-depth profile that is observed in Bangladesh and the authors postulated that some unknown mineral was responsible for lowering the As concentration at depth. While the details remain uncertain, it is clear that the release of arsenic is a very general, natural phenomenon that varies in magnitude but that does not call for truly exceptional conditions.

We found a negative correlation between As and redox potential in the groundwaters from the Special Study Areas (albeit a weak correlation), as well as negative correlations with SO₄ and U. This is consistent with reduction being important. The highest As concentrations were also found where As(III) is the dominant dissolved species. These

observations all indicate that high As concentrations occur in the most reducing groundwaters, rather than those affected by oxidation. Data from our piezometers show that arsenic concentrations tend to be low in the shallowest, most oxidised horizons.

Although only limited S isotope data are available, enriched δ³⁴S compositions (>10 ‰) in the low-SO₄ waters from the Special Study Areas suggest that the SO₄ present represents the residue after sulphate reduction rather than a product of pyrite oxidation. Arsenic-affected groundwaters also sometimes show evidence of H₂S and CH₄ gas, both indicative of strongly reducing conditions.

Major irrigation programmes in Bangladesh are concentrated principally in the drier north-west, and seasonal groundwater drawdown is consequently greatest in this area. All other things being equal, pyrite oxidation would be expected to be greatest in the north-west since this is where the greatest volumes of freshly exposed sediments are found. This spatial pattern of groundwater fluctuation does not fit with the map of groundwater As contamination. In the low-lying part of the delta worst affected by As, seasonal groundwater-level fluctuations are less extreme and water levels are typically much closer to the ground surface.

The evidence overwhelmingly indicates that sulphide oxidation is *not* the major cause of As release in Bangladesh. However, wherever sulphate concentrations exceed those expected from rainfall, pollution and residual seawater, some sulphide oxidation is indicated and some resulting arsenic release may have occurred. The most likely place for this to take place is in the unsaturated zone above the redox boundary. Dug wells are a likely source of such partially oxidised waters and sometimes show high sulphate concentrations and yet from our experience, and that of others, usually give low arsenic concentrations. The young sediments in the Jamuna (Brahmaputra) valley in northern Bangladesh also commonly give rise to relatively high sulphate and high iron shallow groundwaters and may reflect some pyrite oxidation. Nevertheless, the arsenic concentrations are low in these higher sulphate waters. Therefore, even where there is a possibility of pyrite oxidation occurring, it does not appear to give rise to high-As groundwaters.

The evidence is therefore overwhelming that arsenic-affected groundwaters in Bangladesh are usually strongly reducing. This does not prove that the reducing conditions are either necessary or driving the releasing of arsenic. The two factors might just be related. For example, Appelo (personal communication, 2000; www.xs4all.nl/~appt/co2_hfo) has argued that the increase in bicarbonate concentrations found in going from surface water to groundwater could account for the release of sufficient As to give the observed groundwater concentrations. Bicarbonate concentrations are high, often very high, in Bangladesh (and other arsenic-affected areas) and these ions will undoubtedly compete with adsorbed As(V) species to some extent. The question is whether this is sufficient to account for the release of arsenic, particularly since As(III) is also the dominant species in many of the arsenic-affected Bangladesh groundwaters. Our *Special Study Area* investigations showed that there was a positive correlation between arsenic and bicarbonate in Chapai Nawabganj

(especially amongst the earliest set of data which was biased towards the more highly contaminated tubewells) while in Lakshmipur and Faridpur the overall correlation was poor. There are some groundwaters with high bicarbonate and low arsenic concentrations. It appears that bicarbonate competition is one factor but not the only factor, or even the dominant factor, involved in As release.

As demonstrated elsewhere (Chapter 12), the change in oxidation state of As from As(V) to As(III) may also release some As by reductive desorption. Burial of sediments leads to many correlated changes – open to closed systems, mineral dissolution and precipitation, ion exchange, sorption–desorption, new microbiological environment etc. – and it is not possible to look at the changes in terms of any one process. We have already raised the possibility that diagenetic changes in the nature of the iron oxides following burial may be important. This is pure speculation – there is no direct evidence that it is important but it could be, and at least should be considered along with the other possible mechanisms. There is clearly ‘new science’ to be learned.

Ultimately, an understanding of the precise sequence of events leading to the high arsenic concentrations will only be convincing when a full quantitative geochemical transport model can explain all of the major features. At present, the necessary geochemical characterisation of the sediments and the chemical speciation and transport models needed are not yet either known or reliable enough to give convincing, quantitative predictions. This is especially true of the competitive adsorption reactions which are difficult to predict accurately and which are likely to be important. The situation should change in the next few years as the large amount of research begun as a result of the present groundwater arsenic problems worldwide begin to bear fruit.

13.9.7 Role of reductive dissolution

As discussed above, the evidence for the direct involvement of reduction is strong though not yet overwhelming. Nevertheless, studies of the release of arsenic and phosphorus by reduced sediments and soils elsewhere provide support for the reduction hypothesis. Nickson et al. (1998) proposed that reductive dissolution of arsenic-rich iron oxyhydroxides was the principal source of arsenic in the ‘Ganges’ delta aquifers and while this is indeed one likely mechanism, we suspect that it is not the sole mechanism responsible for arsenic release. Some groundwaters contain more As than Fe (on a weight and molar basis) which hints at desorption being an important process although it does not definitely prove it. Our model calculations (Chapter 12) also suggest that other processes could make an even greater contribution to the arsenic release than reductive dissolution which in terms of congruent dissolution would be expected to release only minor amounts of arsenic.

The most highly contaminated water sample from the Chapai Nawabganj hot spot contained 2.3 mg L^{-1} As_T, mostly as As(III), and only 0.17 mg L^{-1} Fe. The most highly contaminated sample from the National Survey contained 1.67 mg L^{-1} As_T and only 0.19 mg L^{-1} Fe. This could only be achieved by reductive dissolution if it was

also combined with extensive Fe precipitation (as a sulphide or carbonate) or with substantial groundwater movement leading to the chromatographic separation of the As and Fe.

It could be argued that reductive dissolution should lead to a good correlation between dissolved iron and dissolved arsenic, as found in some studies of soils and sediments. While there is usually a statistically significant correlation between As and Fe in groundwaters from arsenic-affected areas, this is often far from perfect and indeed is not to be expected even when reductive dissolution is the key process involved in arsenic release. For example, there is no guarantee that the source oxide minerals have a constant As/Fe ratio, especially when the groundwaters are derived from a large geographical area.

We have shown (Chapter 12) that congruent dissolution of oxides is unlikely to be the main mechanism of arsenic release. We suspect and expect that desorption of arsenic is important although this is difficult to prove without detailed laboratory experiments. Desorption is inextricably tied up with reductive dissolution and the two processes are likely to occur simultaneously. Certainly adsorption/desorption of arsenic and of many other elements on metal oxides is well documented, especially for iron oxides. Desorption differs significantly from simple reductive dissolution in that it does not necessarily involve reduction, arsenic can be released without any concomitant release of iron, and unlike dissolution, desorption is very sensitive to many solution parameters including pH, redox status, and the speciation of the groundwater including the concentrations of As(III), As(V), phosphate, silicate, bicarbonate, DOC, calcium and magnesium, for example.

Any process that causes a substantial increase in the concentration of any of these specifically adsorbed species is likely to have an impact on the other adsorbed species. This can occur both by direct competition for adsorption sites as well as through indirect electrostatic effects. These interactions impart a strong positive correlation between many groundwater parameters making it difficult to know which process is ‘driving’ the release. Possible geochemical processes driving the change could involve induced pH and redox changes, the leaching of phosphate fertilisers, phosphate and silicate mineral dissolution, organic matter oxidation with bicarbonate production and phosphate and arsenic release, carbonate dissolution and mineral dissolution and diagenesis.

Reductive desorption of As due to a change in the oxidation state of As from As(V) to As(III) is expected from model calculations (DPHE/BGS/MML, 1999). However, calculations (Chapter 12) suggest that this may not be true in the presence of substantial quantities of phosphate. The amount of As desorption is also sensitive to the surface properties of oxide minerals such as their surface charge, surface area (particle size) and surface structure.

The diagenetic changes that occur and on changing from an oxidising to a reducing environment are not well understood for the iron oxide minerals present in Bangladesh sediments, or indeed more generally for Fe(III) oxides in other reducing environments. However, it is reasonable to speculate that there could be significant surface and structural changes following sediment burial and the

rapid imposition of anaerobic conditions. Ageing of fresh hydrous ferric oxide (Hfo) is a natural process that has been demonstrated in the laboratory and in natural sediments. This involves an increase in particle size, reduction in surface area and a change in bulk and surface structure. Some ageing even occurs under oxidising conditions. This ageing process is likely to lead to some As release but some As is also likely to be permanently occluded in the structure of the evolving solid phase. This needs to be understood better. The bulk chemistry of iron oxides is also important since some of the As in naturally-occurring iron oxides is likely to be present as a solid-solution and thus unavailable for rapid release.

13.9.8 Role of organic matter

Organic matter undoubtedly plays an important role in the development of the high-As groundwaters in Bangladesh. It can do this in three principal ways: (i) solid organic matter buried with the river sediment could be a *source* of As that is released when the organic matter is oxidised (like phosphate); (ii) dissolved organic matter could help to *mobilise* adsorbed arsenic through its interactions with mineral (oxide and clay) surfaces; (iii) *indirectly* through redox processes – the microbiological oxidation of organic matter, especially of the young, labile organic matter present in freshly buried sediments, imposes the strongly reducing conditions that lead to many other transformations.

The relative importance of these three processes is difficult to judge at present. As with all discussions about the reasons for the high-As groundwaters, the relatively small mass transfers required from solid to solution phase make it difficult to rule out many potential sources. Quantification is required.

While buried peat deposits are occasionally found in Bangladesh sediments, most sediments contain only small amounts of organic matter, usually less than 1% C. If we assume that the sediment at burial contains 1% C (2% organic matter) and that this organic matter contains 5 mg As kg⁻¹, then this will contribute 0.1 mg As kg⁻¹ to the sediment arsenic load, a significant but generally minor proportion of the total load. Nevertheless, since it will be released when the organic matter is oxidised, it could contribute to the arsenic in groundwater. It all depends on the extent of oxidation, the As content of the original organic matter and the size of potential sinks.

High DOC concentrations are characteristic of many high-As groundwaters in reducing environments (e.g. Taiwan, Hungary and China) but it is not known whether this is incidental, a characteristic of groundwaters in young sediments undergoing rapid diagenesis, or bears a stronger causal relation. The DOC concentrations of Bangladesh groundwaters are typically slightly higher than for average groundwaters but usually not exceptionally so, and certainly lower than found in most soil pore waters. The interactions of DOC with adsorbed As(III) and As(V) are poorly understood quantitatively and need to be studied in more detail.

The development of reducing conditions appears to be an important precursor to the release of arsenic, and this is undoubtedly related to the oxidation of organic matter. It is also reflected in the high bicarbonate concentrations of

many of the As-affected groundwaters. While it could be anticipated that the greater the organic matter content, the greater the tendency for strongly reducing conditions to be created, the relationship is unlikely to be that straightforward. Other factors, particularly the 'biological availability' of the organic matter, are likely to be important. Young soil organic matter is likely to be more reactive than older organic matter such as that in peats.

13.9.9 Iron-rich groundwaters and arsenic

Iron-rich groundwaters are common and are found throughout the world. If all such waters contain excessive concentrations of arsenic, then the problems that have occurred in the Bengal Basin and elsewhere would probably never have happened. It is simply not correct to equate iron-rich groundwaters with arsenic-contaminated groundwaters. There are many iron-rich groundwaters which contain very low concentrations of arsenic as for example in many UK groundwaters. We found that even in Bangladesh, the overall correlation between the iron and arsenic concentrations in groundwaters from the shallow aquifer was not particularly good although there is undoubtedly sometimes a 'statistically significant' correlation especially on a local scale. The deep aquifer in Lakshmipur gave iron-rich groundwaters and yet these were low in arsenic. There are also other environments in which severely arsenic-contaminated groundwaters occur which are not iron-rich. Iron-rich groundwater is one 'risk factor' but there are other factors involved.

13.9.10 Contamination of the deep aquifer

The evidence from our National survey showed that some 5% of the sampled deep wells (i.e. wells greater or equal to 150 m depth) exceeded the WHO guideline value for arsenic and 1% exceeded the Bangladesh standard. However, most of these deep wells had been installed to avoid salinity problems in shallower groundwaters and were mostly from the southern coastal region of Bangladesh. The statistics cannot therefore be applied to other parts of Bangladesh and it is clear that a systematic study of the deep aquifer in other parts of Bangladesh is required. Exactly at what depth such low As groundwaters are found is not certain since there are not many wells in the deeper parts of the shallow aquifer. This relationship is likely to vary in different parts of the country depending on the depositional history (Chapter 3). However, the statistics that do exist (Chapter 6) suggest that wells will often need to exceed 150 m depth to access low As groundwater.

There is considerable confusion in Bangladesh over the use of the word 'deep' in the context of 'deep well' and 'deep aquifer'. A 'deep well' can refer strictly to the depth of the well, as in this report, with cutoffs usually given at 150 m or 200 m. It can also refer to the type of well construction, i.e. irrigation wells are often described as 'deep wells' even though they are usually placed in the lower part of the 'shallow' aquifer. These wells are designed to deliver a greater yield than ordinary hand-pump tubewells and are consequently larger diameter and are often drilled by reverse circulation as opposed to the 'sludger method' used for most domestic supply hand-pump tubewells. The

irrigation wells are usually fitted with removable diesel pumps. Even a strict 'depth' classification can be confusing since with deep wells, the screened interval may not be placed at the bottom of the well. It is the location of the screened interval that is of greatest interest.

Use of the terms 'deep' aquifer and 'shallow' aquifer implies that there are two distinct aquifer units separated by a substantial aquiclude (clay layer). This is not necessarily the case as we found in Faridpur. The presence or absence of an aquiclude has important implications for the long-term sustainability of low As deep wells, and therefore needs to be better understood across Bangladesh.

It is often heard in Bangladesh and neighbouring West Bengal that deep wells have been found to be contaminated. It is also frequently said that deep wells that were originally arsenic-free have become contaminated in a matter of a few years. In view of the possible role that deep wells could play in the long-term supply of safe drinking water in Bangladesh, such assertions need to be established beyond doubt and if substantiated, the reasons need to be understood. This means that the data need to be put in the public domain and open to peer review. This includes both the analytical data and information about the sampling methodology and well construction. These observations of contaminated deep wells are so important that they need to be confirmed, preferably by independent scientists.

It is also important to distinguish between whether it is the well that is contaminated or the aquifer. A deep well may be contaminated because shallow, contaminated groundwater has been drawn down either as a result of drawdown in the aquifer induced by pumping or of inappropriate well construction resulting in some form of short-circuiting close to the well casing – this distinction is obviously important and will require a detailed case-by-case investigation of affected wells to resolve. It is also sometimes the case that deep wells have multiple screened intervals to increase productivity which means that the contamination could be derived from the shallower interval. Also, where only a relatively small percentage of wells are found to be contaminated, there is scope for various errors to creep in – including errors in sampling, analysis and reporting. There is sometimes confusion over feet and metres, for example.

13.9.11 Source of high phosphate concentrations

Bangladesh groundwaters contain unusually high phosphate concentrations for groundwater – a median concentration of 0.3 mg L^{-1} , an average concentration of 0.75 mg L^{-1} and a maximum concentration of 18.9 mg L^{-1} from our National Survey ($n=3530$). The variation is also large but not as great as for arsenic (in a relative sense).

From a geochemical point of view, explaining the high phosphate concentrations is every bit as much of a challenge as explaining the high arsenic concentrations. Therefore not surprisingly, the source of the phosphate is also the subject of differences of opinion. Some for example believe that it is derived from phosphate fertilisers or from degradation of organic matter (e.g. Acharyya et al., 1999, 2000). However, the evidence points to a natural non-fertiliser source. Phosphate transport from the surface can be expected to be retarded to some extent and therefore quite

slow. Yet a substantial number of deep wells (depth greater than 150 m) contain high phosphate concentrations (greater than 1 mg L^{-1}). These deep waters are also likely to be several thousand years old and therefore will predate the use of fertiliser. If leaching of fertilisers were the principal source of phosphate, phosphorus concentrations should be a maximum at shallow depths. Our piezometer data indicate that, if anything, phosphorus concentrations in the shallow aquifer tend to increase with depth. High P porewaters are also found in sediments far from fertiliser inputs and in diverse geochemical environments (lakes etc). Also, if fertilisers were an important source of phosphorus, dug wells should show high phosphate concentrations since they are the shallowest of wells (albeit somewhat displaced from agricultural activity). Again, our limited data from Chapai Nawabganj show the reverse. Of course, phosphate derived from fertiliser leaching is a possibility in some shallow groundwaters but this should not be confused with the more general situation relating to the typical high-P and high-As groundwaters of Bangladesh.

The decomposition of organic matter will undoubtedly release some phosphate (and arsenic) into solution. The Redfield formula gives the molar C/P ratio as 106 (based on algal organic matter) and so assuming a closed system and that half of the bicarbonate in a bicarbonate-rich water (say $610 \text{ mg L}^{-1} \text{ HCO}_3^-$) has been derived from organic matter decomposition, this would release $1.5 \text{ mg L}^{-1} \text{ P}$. Much of this is likely to be re-adsorbed by the oxides present in the sediment as reflected by the large concentrations of oxalate-extractable sediment P (Figure 11.15). In practice, some CO_2 will have been lost to the atmosphere and so the extent of oxidation will be greater than this. Therefore while oxidation of organic matter will contribute to some of the dissolved P, it is unlikely to supply it all especially in the high-P waters found in Bangladesh. Data from our Special Study Areas do not indicate a significant correlation between bicarbonate and phosphate, further weakening the case for organic matter being the dominant source of dissolved P. While the arsenic content of organic matter is unknown, similar arguments can probably be applied to arsenic. Certainly there are groundwaters with high bicarbonate concentrations and low arsenic concentrations (e.g. dug wells, Faridpur 'deep' wells).

Rather we believe that the phosphorus is predominantly of natural, inorganic origin, rather like the arsenic. While there is not a very strong correlation between arsenic and phosphorus concentrations in individual wells, the National Hydrochemical Survey and maps show a somewhat similar spatial distribution with the highest phosphorus concentrations in the south and east of Bangladesh where the arsenic concentrations are also highest. Chromatographic separation resulting from groundwater flow, especially separation of As(III) and P, could contribute to the generally poor As-P correlation observed on a well to well basis.

Therefore, as for arsenic, some of the phosphate could well be derived from reductive dissolution of, and desorption from, iron (and other) oxides. Indeed, according to the iron oxide reduction hypothesis, it would be surprising if elevated phosphorus concentrations were not observed in the high-arsenic areas. However, unlike arsenic, no change in oxidation state of the phosphorus takes place

and so reductive desorption does not contribute to phosphate release suggesting that the other processes (dissolution, oxidation of organic matter, competitive interactions and diagenetic changes to the oxides) may be important.

There is evidence from the phosphorus and sodium maps of some spatial correlation between the two and so seawater or buried shell-material from marine sediments could be another possible source. Apatite has been observed in the sediments. Biotite is a further possible mineral source – Bangladesh sediments contain abundant biotite – but since biotite weathering is accelerated by the oxidation of structural Fe^{2+} it would be expected to be greatest in the shallowest horizons above the redox boundary. As mentioned above, the field data indicate a deeper source.

The pyrite oxidation hypothesis for arsenic release is less attractive for explaining the high phosphate concentrations. While arsenic has both siderophilic (metal-loving) and chalcophilic (sulphur-loving) tendencies, phosphorus is more strongly siderophilic and therefore would not be expected to be released in great quantities from pyrite oxidation. We could find no data for the phosphorus content of pyrites to confirm this, but expect it to be quite low.

13.9.12 Depth relationships

Arsenic in groundwater in Bangladesh increases with depth
Nickson et al. (1998)

Despite the assertions made by Nickson et al. (1998), the As concentrations in groundwater do not always, or even generally, simply increase with depth. A bell-shaped arsenic-depth relationship is much more likely and when appropriate measurements have been made, this is what is observed – as with our piezometers, for example. Very shallow wells (say within 5 m of the water table) tend to have quite low concentrations and deep wells tend to have very low concentrations with intermediate depths having variable but higher concentrations of arsenic. In contaminated areas, arsenic concentrations in groundwater tend to increase most rapidly within 10–20 m of the surface. The exact relationships are likely to be more closely related to the depth below the water table rather than the ground surface, and the extent of annual water table fluctuations. Other factors, such as variations in the ‘source term’ and in the geochemical environment, will also play a role and so simple, generally applicable As–depth relations are unlikely especially when viewed at a particular site.

There are therefore horizons where arsenic increases with depth and horizons where it decreases with depth. In the shallowest horizons, sediment-water interactions are less advanced and there is likely to be a zone of active flushing where any arsenic released will tend to have been washed away. Furthermore, according to the iron oxide reduction hypothesis, the strongly reducing conditions necessary for arsenic release will not have been fully established close to the surface. Hence groundwater As concentrations will tend to be low. Below the redox boundary, As concentrations can be expected to increase. This has been observed in studies of lake and ocean sediments.

In the deepest horizons, the sediments will be older and any arsenic released will tend to have been flushed

away perhaps at a time when the sea level was much lower and strong flushing of the aquifer was more likely. Also, if as we suspect, arsenic release is in part at least, a response to the sudden imposition of reducing conditions on freshly buried sediments, then older sediments with their older and less labile organic matter will be less able to maintain the strongly reducing conditions required.

In intermediate horizons, groundwater As concentrations can be expected to vary up or down depending on local variations in the As source, mobilisation and transport terms. For example, they may reflect local variations in the iron oxide content of the sediments at the time of burial (source term), or the redox status depending on the organic matter content (mobilisation term), or the degree of flushing depending on the permeability of the strata, the hydraulic gradients and the local groundwater flow patterns (transport term). There is evidence from our studies in Mandari of strong water quality stratification of the shallow aquifer pointing to the importance of these local variations.

In terms of understanding the processes involved as a function of depth, it can be confusing to mix data for wells drilled at different depths but from different places. Sets of piezometers at the same location but at different depths, as used in this study, are a better way of understanding such relationships.

13.9.13 Hand-dug wells, tubewells and when the arsenic was released

We know of no difference in the inorganic and organic quality of water from tubewells and hand-dug wells. Both extract water from subsurface geological formations i.e., groundwater and from about the same depth.

From ‘Groundwater Arsenic Poisoning And A Solution To The Arsenic Disaster In Bangladesh’, by Thomas E Bridge:
www.bangladesh-web.com/news/jan/14/fv4n104.htm
(downloaded 17 July, 2000).

Dug wells at a given depth should give the same water quality as tubewells from the same depth

The beginning of poisoning does appear to have occurred after the drilling of the tubewells.

The absence of reported poisoning prior to the nineteen eighties supports the theory that the poisoning of the groundwater is recent.

See Thomas E Bridge and Meer T Husain, ‘The Increased Draw Down And Recharge in Groundwater Aquifers And Their Relationship to the Arsenic Problem in Bangladesh’, undated article;
www.dainichi-consul.co.jp/english/arsenic/article/meerarticle6.html (downloaded 17 July, 2000).

A criticism of the DPHE/BGS/MML (1999) Phase I report was that we suggested that the arsenic had probably been in the groundwater for a long time, whereas Bridge and Husain say that this is contrary to historical medical evidence. In particular, they could not understand why hand-dug wells which were widely used in the past should be different from modern tubewells from a similar depth. They stated that it would be ‘illogical to find hand dug wells are uncontaminated and tubewells are contaminated in a similar geological, hydrological and geochemical conditions’.

This is a basic misconception. Groundwater abstracted

from hand-dug wells and tubewells at the same depth can have very different arsenic concentrations precisely because of the different hydrological and geochemical conditions. Our 1997 findings from two dug wells in the highly contaminated region of Chapai Nawabganj showed that these both had low arsenic concentrations. We suggested that this was probably due to more oxidising conditions in the hand dug wells or to the lack of contact of the shallowest groundwaters with arsenic-bearing strata.

It seems perfectly reasonable to us to expect that the redox conditions in a large diameter open well will be different from those of a tubewell at a similar depth. Since we believe that strongly reducing conditions are probably required for arsenic release in Bangladesh, it makes sense that there could be real differences between arsenic concentrations in water from dug wells and tubewells. Much other evidence from Bangladesh and West Bengal now confirms this, including our more recent results from the piezometers in Chapai Nawabganj.

The introductory quotes have been used to support the idea that since dugwells are expected to have the same water quality as tubewells, and since tubewells are contaminated now and yet there were no arsenic patients until recently, the arsenic could not 'always' have been present in the groundwater but must be a recent phenomenon. It has been suggested that the construction of the Farakka barrage on the River Ganges has led to the oxidation of pyrite and thereby caused the high As groundwaters now observed in Bangladesh (and West Bengal?). As indicated under the discussion of sources given above, there is no evidence to support this rather tortuous hypothesis.

Air can diffuse freely down a dug well and so it is likely that conditions will be more oxidising at the base of a dug well than in a tubewell of a similar depth. This is borne out by observations of many redox-sensitive parameters such as dissolved oxygen, nitrate, ammonium and sulphate. The nature and extent of any lining of the dug well could have an influence on the redox conditions at the base of the well, and hence on arsenic concentrations. Allowing, and even promoting, aeration in the immediate vicinity of the dug well may therefore be beneficial. It is also inappropriate to mix data from dug wells with data from tubewells when examining As-depth relationships.

Before the drilling of tubewells, drinking water in Bangladesh was derived from surface water ponds and from dug wells, both now known to be sources of relatively low-arsenic water (and high levels of bacterial contamination). Therefore the apparent overlap of tubewell use and the recognition of symptoms is perfectly understandable since the tubewell water is the principal source of the arsenic!

This says absolutely nothing about exactly when the 'groundwater was poisoned' (other than it was before it was drunk!). Our 'dating' of groundwaters provides some indication of when the contamination may have occurred. For example, we have found some shallow groundwaters which have very low tritium concentrations yet high arsenic concentrations. This suggests that the source of the arsenic predates the 1960's. Experience of arsenic release in soils and sediments elsewhere suggests that some arsenic release can occur very rapidly after sediment burial and the development of strongly reducing conditions. It often takes about two weeks for reducing conditions to

become established in recently-flooded soils, for example. Desorption processes tend to be very rapid (usually in seconds to days) and so the initial As release could have occurred within a matter of weeks following burial. There is also likely to be a slower release related to further burial and the development of strongly reducing conditions, to oxide mineral dissolution, clay mineral weathering and to slow, diagenetic changes to the structure of the minerals which sorb As. It appears that in Bangladesh further arsenic release occurs as the sediments become more deeply buried (or older) such that the highest groundwater arsenic concentrations are frequently found in the 20–30 m bgl depth range.

We are not sure of the relative importance of these fast and slow release mechanisms. We believe that much of the arsenic was released thousands of years ago rather than recently. However, this does not mean that there will be no changes to the arsenic concentration in well water. Movement of groundwater, either reflecting natural groundwater gradients or those induced by pumping, will also lead to the movement of arsenic. Some wells will increase in concentration with time, some will decrease. In the very long term, at timescales well beyond those of significance to the present management of the aquifers, arsenic concentrations can be expected to decrease as fresh water flushes away the arsenic that has been released. Since the arsenic release is essentially a one-off response to the dramatic change in geochemical environments following burial, further release is not expected.

Not surprisingly, the time when groundwater began to be exploited for drinking water also coincided with the time when groundwater began to be heavily exploited for irrigation. However, there is no evidence to connect directly the onset of widescale irrigation with the onset of arsenic poisoning. However, others continue to speculate that 'excessive' groundwater abstraction for irrigation and the use of phosphate fertilisers are prime causes of the groundwater arsenic problem (Acharyya et al., 2000).

It is also often said that some tubewells had been in use in Bangladesh long before, perhaps 60–70 years before, the recent rapid expansion of the 1970's and later. Yet 'there were no arsenic patients then'. Two points: firstly, who says that nobody suffered from chronic arsenic poisoning in those early days and secondly, what is the evidence for such a statement? Although tubewells were undoubtedly used before the recent expansion, the number in use was much, much smaller than at present. Therefore, the number of arsenic-affected individuals would have been correspondingly far fewer and would probably have gone undetected especially since the symptoms would not have been widely recognised.

13.9.14 Borehole logging and borehole licensing

Despite the very large number of tubewells drilled in Bangladesh, it is still difficult to form a reliable 3-dimensional picture of the aquifers both at the regional scale and the local scale. This is because most of the domestic tubewells have been drilled by private contractors using the sludger (hand flap) method and there is no requirement or system to record details of the borehole logs on completion. Even details of most of the government-drilled tubewells are not

readily available. This is understandable given the large number of shallow tubewells but there is a case for all deep tubewells to be licensed by the government and for details of the borehole logs to be lodged in a systematic way. This could form a beginning to an aquifer protection policy for the deep aquifers. Some incentive would probably need to be given to private contractors to make such a notification scheme work.

It would be very useful to always record the lithological variations with depth (sand, silt, clay, peat etc.) and the colour of the sediments (grey, brown etc.). The texture is obviously important in terms of potential groundwater yield but can also yield valuable information about the depositional environment. The colour is useful since it reflects the oxidation state (and maybe age) of the sediments. For example, a change from grey to orange-brown may help to identify the Holocene-Pleistocene boundary.

13.9.15 Moratorium on drilling of all new shallow wells

There is certainly a good case for having a moratorium on the drilling of all new shallow wells in the arsenic 'at risk' areas. New wells add to the burden of an already large testing programme. DPHE have halted all such drilling activity but the installation of private wells continues. The justification for a moratorium is partly economic – if the probability of the new well being contaminated is 50%, then the cost of drilling a well with acceptable quality will actually be double that of drilling a single well. Other alternatives may then become more attractive. In practice, in order to provide a clear and unambiguous message, it would be best if there was a complete cessation on the drilling of all new wells in the shallow aquifer for the time being throughout Bangladesh even though there are areas in northern Bangladesh where the shallow aquifer does not pose a threat. Sharing of water from certified 'good' wells would be a better interim solution and would be a simple message to convey – 'a bottled water distribution system without the bottles', i.e. use any approach to the distribution of safe drinking water that works.

There are also other potential constraints on the use of hand-pump tubewells in the shallow aquifer. These constraints may become more serious in the future (Figure 13.3). The decline in water table during the latter part of the dry season may put increasing numbers of suction hand pumps out of reach of the water table, especially in the uplifted Pleistocene Tract areas. Salinity is a problem in the coastal region. Even in areas where 'no constraints' are indicated such as the Chittagong Hill Tracts (Figure 13.3), the ground may be unsuitable for the widespread development of hand-pump tubewells. The arsenic constraint is very widespread throughout Bangladesh, especially if a lower limit than the present Bangladesh standard is sought (which should be the long-term aim). When this is combined with other chemical constraints, particularly of manganese, it is hard to avoid the conclusion that the shallow aquifer in Bangladesh is largely unsuitable for drinking water supply.

Naturally there has been something of a backlash against the use of all groundwater in Bangladesh. Certainly the arsenic issue, indeed all water quality issues, would be easier to manage and monitor if far fewer wells were used

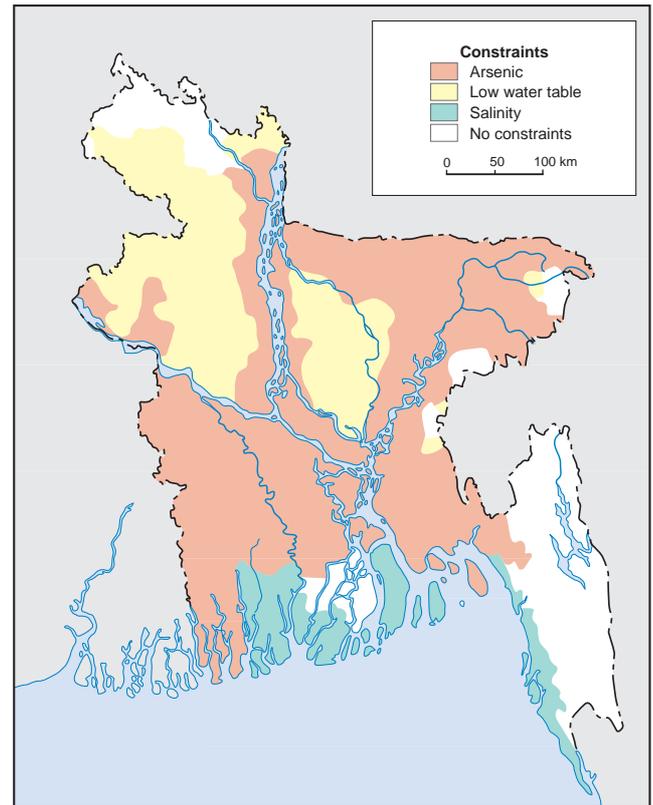


Figure 13.3. Map showing possible constraints on the future use of hand-pump tubewells (after NWMP, 2000).

for drinking water. Ideally there should be a trend away from individual tubewells towards a smaller number of wells with a local distribution network perhaps in the manner suggested in NWMP (2000). The water could then be more easily treated for arsenic, iron and manganese, if necessary, and more easily monitored. Low-arsenic deep-well groundwater could also be used as primary source of drinking water. There is no reason to dismiss the use of all groundwater in Bangladesh just because of the water quality problems in the shallow aquifer. Groundwater provides a valuable source of drinking water in many parts of the world, and will continue to do so. The water quality needs to be assessed objectively on a case-by-case basis. Surface water is not without its own problems. Existing shallow tubewells can continue to be used for washing etc.

The case for the drilling of deep wells in contaminated areas such as the south-east of Bangladesh is strong since the available evidence is that these often provide good-quality drinking water, albeit at an increased cost. However, there are important questions about the way that deep boreholes are constructed and more generally about the long-term sustainability of deep groundwaters. These questions are currently being addressed by the DPHE and others. Experience of using deep wells in the southern coastal region of Bangladesh over many years has shown that the quality of the deep groundwater there has not deteriorated as a result of the leakage of saline water from shallower depths. The same should be true of arsenic in this area at least.

Providing that the wells are properly sealed during con-

struction in order to prevent rapid vertical leakage down the borehole, that no shallow horizons are screened to increase productivity and that the aquifer has a reasonable layer of clay separating the shallow and deep aquifers, there is every reason to expect that the water quality should remain good for the life-time of the well. This is because there are few driving forces for chemical change at depth (in terms of chemical gradients). We also know from carbon dating that the deep waters are often several thousand years 'old' and from modelling that natural groundwater flow is slow. Why should conditions suddenly change when tapped by a small well? Nevertheless we are conscious of contrary information coming from elsewhere (but have not seen the data and detailed background), particularly from West Bengal, and so we advocate that all deep wells used for public supply are monitored for arsenic at regular intervals, say every 6 months for at least five years and perhaps for ever, to ensure that any adverse trends are quickly identified. Hopefully, there will be improvements in arsenic testing procedures that will make such monitoring more feasible for Bangladesh.

The main impact of deep wells is likely to arise where shallow water of very different quality is induced to flow to the deep aquifer as a result of irrigation pumping or the use of some other high-capacity pump. Not surprisingly, our modelling (Chapter 5) indicates that installing high capacity wells at depth will induce some groundwater flow from shallower horizons and may therefore slowly increase arsenic contamination at depth. There needs to be a groundwater protection policy for the deep aquifer. This should consider any possible impacts of abstraction on the movement of the saline-freshwater boundary in the southern coastal region.

13.9.16 Toxicity of different arsenic species found in groundwater

Arsenic can exist in various forms in groundwater. The two dominant 'species' are arsenate (oxidised form) and arsenite (reduced form). Various forms of organic arsenic can be found in surface waters but there is no evidence that they exist at significant concentrations in groundwater. The proportions of arsenite and arsenate found in Bangladesh groundwaters appear to vary greatly although this needs confirming. More work needs to be done on reliable methods for preserving As species and for speciating arsenic in Bangladesh (and other) groundwaters. Certainly much of the As in Bangladesh aquifers is in the reduced valence state as arsenite species. There are a number of projects investigating both the solid and solution phase speciation of As in Bangladesh aquifers and the situation should be much clearer in the near future.

It is often stated that arsenite in drinking water is considerably more toxic to humans than arsenate. This appears to be based on studies with micro-organisms. There is no evidence that this is the case with humans. Arsenate is rapidly reduced to arsenite in the human gut. This makes the setting of drinking water standards and the testing of arsenic relatively straightforward. Measurement of total arsenic should be adequate. No existing national drinking water standards attempt to differentiate between the different forms of arsenic, neither does the WHO

guideline value.

13.9.17 Relationship between number of arsenic patients and groundwater quality

Low level arsenic poisoning is a chronic disease and there is a lag time before symptoms become apparent. This delay or latency is typically about 10 years from first exposure to the development of skin lesions, particularly keratoses and more than 20 years for skin cancer (Smith et al., 2000). The present-day concentration of arsenic in drinking water is therefore only one factor to be considered when comparing maps of arsenic in drinking water with maps of the known incidence of arsenic-related diseases. Many of the wells in Bangladesh are less than 10 years old. We found that 68% of shallow wells sampled in our NHS had been constructed in 1990 or later. The percentage in Mandari was even greater. Rapid action now could therefore save a lot of suffering in the next 10–20 years.

All other things being equal (which is not necessarily the case), the first patients to be diagnosed will tend to be those who have been drinking highly contaminated water for the longest time. These will have been located precisely because they developed symptoms, i.e. not by random survey. The most commonly quoted figure for the number of people affected by skin lesions and arsenicosis in Bangladesh is 8000 although it is unclear exactly how this figure was derived. It is likely to be an underestimate. It is certainly a very small number in relation to the total number of people exposed to arsenic contamination. A more recent estimate of the number of people in Bangladesh 'affected by arsenic and suffering from arsenic dermatitis (Black spots, eruptions and even cracking of skin)' is 150,000 (from www.sdnbd.org/dphe_profile.htm). It is not clear whether this number includes estimates of those with as yet undiagnosed problems such as internal cancers. Smith et al. (2000) say that for Bangladesh, 'estimates indicate that at least 100,000 cases of skin lesions caused by arsenic have occurred and there may be many more'.

Experience from elsewhere suggests that the lifetime risk of developing skin cancer from the ingestion of $1 \mu\text{g As per kg body weight per day}$ (roughly equivalent to 1 L d^{-1} at a concentration of $50 \mu\text{g L}^{-1}$) is 1 per 1000 to 2 per 1000 (Smith et al., 2000). Skin cancers are usually not fatal if treated appropriately. In other countries, the main causes of death associated with chronic ingestion of arsenic in drinking water are internal cancers. The risk of getting any type of cancer at the $50 \mu\text{g L}^{-1}$ level of exposure could easily be as high as 1 in 100 (Smith et al., 2000).

Patients from the Chapai Nawabganj hot spot area were in some cases consuming water containing in excess of $1000 \mu\text{g L}^{-1}$ As. This concentration is not typical of Nawabganj district as a whole and is the exception rather than the rule. In this respect, our arsenic maps, especially the smoothed map, may be confusing since they emphasise the typical rather than the exceptional. Even though much of northern Bangladesh plots in the lowest probability class interval used (<0.1) in our smoothed probability maps (Chapter 9), this does not imply that the area is essentially uncontaminated. A 10% chance of drinking As-contaminated water is still a very high probability. More tellingly, the mean groundwater concentration (represent-

ing a measure of the mean dose) is more than two orders of magnitude lower in parts of northern Bangladesh compared with the worst-affected areas in the south. The chances of drinking As-contaminated water are much lower there and this should be reflected in the strategy adopted of the short-term or emergency mitigation programme.

In the SE of Bangladesh, the mean concentrations in the drinking water are greater but the incidence of arsenic-related diseases is less than in parts of the Ganges valley in west central Bangladesh. The shape of the As frequency distribution is likely to vary in different parts of the country and so the mean As concentration may not provide a good reflection of the number of highly contaminated tubewells in a particular area.

The recently published results of the comprehensive screening carried out by the National Emergency Screening Program (NESP) (BAMWSP, 2000) recorded 3119 patients in 6 *upazilas* which also suggests that the total number of patients in Bangladesh is definitely considerably greater than 8000. There is also a large difference between the large number of patients found in one *upazila* from Chandpur district in the south-east in this survey with the results of a parallel DPHE-UNICEF survey in an adjacent *upazila* in the same district where the number of patients found was very low. The reasons for this difference need to be resolved.

This discussion is complicated by the commonly-held belief that arsenic concentrations in tubewells are increasing with time. Unfortunately the data to support this statement as a general trend have not been presented. Our monitoring results to date do not support such a conclusion but also do not prove that such a trend is not occurring at least over timescales of years, decades or longer. The situation is still unclear. Quantifying small but significant time trends is very difficult and investigations must be carefully planned to separate the various plausible sources of variation – analytical uncertainty, recovery from disturbances due to well installation and diurnal, seasonal and long-term changes. Merely taking a few ad hoc samples at various places and at various times is insufficient to establish such trends reliably. This is clearly an important issue that deserves further attention.

The question of whether there is a threshold concentration of arsenic below which no symptoms are likely to occur (in the lifetime of an individual) is hotly debated. Scientists are currently divided on this. This issue is closely related to the question of the linearity of the dose-response curve. It has significant implications not only for the setting of drinking water standards but also for any mitigation strategy. If the response is linear, merely blending high- and low-arsenic waters may reduce the arsenic concentration to below the accepted drinking water standard but would not reduce the overall incidence of disease. A greater population would be exposed to low, but significant, arsenic concentrations and might therefore suffer from an arsenic-related disease, albeit later in life.

13.9.18 Lessons to be learned

In retrospect, it is clear that mistakes were made in not picking up the groundwater arsenic problem in Bangladesh

earlier, and in not acting on the earliest indications rapidly enough. Smith et al. (2000) recommend that all drinking water sources should be tested for arsenic. In most developed countries, this is now the case for all public supplies but the situation with small, private supplies is less clear. A discussion between the general public, scientists, policy makers, development organisations and funding agencies on what steps might be taken to prevent future 'arsenic' problems arising would be helpful.

There are broader issues to do with drinking water quality standards than arsenic. What other 'surprises' are waiting to be found? How do we find them quickly? The range of potential problem chemicals is very large. As analytical techniques improve, we can measure more determinands at lower levels and gradually gain a greater idea of the risks posed by a broader range of chemicals. However, the cost of a full chemical analysis increases accordingly. Even in developed countries, many small private water sources are not presently tested for the full range of WHO health-related parameters. Some would argue that it would be too burdensome and 'bureaucratic' to require them to do so. The cost would be too great given the perceived risk at the time. In practice, as the cost of a 'full' chemical analysis of a water sample increases, the number of private wells tested is likely to decrease.

There are of course also chemicals that maybe should be on the WHO list, and one day will be, but about which there is not enough information at present to form such a judgement. Various trace organics are obvious examples. Thallium, for example, is already on the USEPA list of contaminants covered by their National Primary Drinking Water Regulations but is not on the current WHO list.

13.10 RECOMMENDATIONS FOR FUTURE RESEARCH

Below we outline a number of topic areas where future scientific research could contribute to the understanding and solution of the groundwater arsenic problem in Bangladesh. These topics are not intended to detract from the number one priority in Bangladesh – to identify all affected individuals and to provide everybody with 'arsenic-free' drinking water rapidly. If there is a shortage of funding, then the more long-term or 'academic' research should take second place. It will probably be done later anyway.

Some of the topics listed below should aid the mitigation programme in Bangladesh directly, others are more generic, require sophisticated laboratories and are best carried out outside of Bangladesh. The suggested topics concentrate on chemical and geological studies. We do not include mitigation, health or social studies although these are of course important. We are also aware that programmes may already be underway for addressing some of the issues outlined below.

Arsenic analysis and field-test kits – reliable arsenic analyses are essential for arsenic testing. There is a need for field-test kits which can detect arsenic in the range 5–200 $\mu\text{g L}^{-1}$ reliably. These should be cheap enough to be available on the local markets. There has been a significant improvement in the design of field-test kits in the last three years and the challenge now is to make these kits widely available and affordable in Bangladesh. Although the development

of accurate field-test kits should not delay the emergency testing and mitigation work (Smith et al., 2000), improvements in the technology will have undoubted medium- to long-term benefits and should reduce the inevitable confusion that will occur when deciding on the long-term suitability of various drinking water sources. It would also be beneficial if the present Bangladesh drinking water standard for As were reduced to the WHO guideline value;

Arsenic distribution with depth in the shallow aquifer – most shallow wells are screened in the shallowest horizons that will guarantee fresh water with an adequate yield. There is a dearth of data about how arsenic concentrations vary below this depth, i.e. in the deeper parts of the shallow aquifer. This should be determined at a number of strategic locations using nested sets of piezometers, or failing that, a suitable downhole water sampler;

Arsenic contamination of the 'deep' aquifer – there are reports of arsenic contamination of the deep aquifer in Bangladesh, and sometimes reports of once arsenic-free deep wells becoming contaminated with time. These are such important conclusions that the facts need to be established beyond doubt as quickly as possible. From our experience of deep wells in southern Bangladesh, the large majority of tested wells are presently very low in arsenic, mostly (but not always) less than $10 \mu\text{g L}^{-1}$. DPHE's experience from their deep well drilling programme is broadly similar.

Therefore all deep wells that are identified as being contaminated ($>10 \mu\text{g L}^{-1}$) should be double checked by resampling and re-analysis. The re-analysis should be carried out by an independent and reputable laboratory, preferably using an analytical method with sensitivity at the low $\mu\text{g L}^{-1}$ level. This testing should be done blind. Until this has been done, such reports should be viewed with caution. It may be worthwhile duplicating all testing of deep wells from the outset, i.e. taking duplicate samples and sending to different laboratories, or maintaining the second sample in a secure place in case re-analysis is called for (rather like the procedures adopted for drug testing of athletes). Professional statistical advice should be sought.

For those deep wells positively confirmed as contaminated in this way, it needs to be established whether the aquifer itself is contaminated or whether the contamination is due to leakage due to poor well design or construction, multiple screened intervals or an error in recording the well depth.

Countrywide availability of the 'deep' aquifer – better maps of the distribution, depth and water quality (arsenic, manganese, iron and salinity, at least) of the deep aquifer are needed over the whole of Bangladesh. This should include an assessment of the thickness of any intervening aquiclude so that hydrogeological modellers can model the flow of water to and through the deep aquifer. We recommend that a PC database is set up containing coded lithological logs from throughout Bangladesh. This should make use of existing data where they are of suitable quality but there will need to be a new drilling programme to fill in important gaps in knowledge.

Sustainability of the deep aquifer and regional groundwater flows – a better idea of the nature of the regional groundwater flows and of the rate of recharge to the deep aquifer are needed.

If a substantial amount of water is to be abstracted from the deep aquifer, then the ability of the deep aquifer to sustain this for 50 years or longer needs to be established. Also the impact that this may have on existing deep flows and on the possibility of further saline intrusion in the coastal region needs to be determined.

Dating of groundwaters and sediments – the ages of the groundwaters and sediments are an important scientific aspect of the arsenic problem and should be systematically studied using a variety of dating techniques.

Detailed village-scale studies – detailed studies of the hydrogeology and hydrochemistry of small areas, say about the size of a village or mouza, should be undertaken to understand better the reasons for the large degree of spatial variability in arsenic concentrations observed. This should include a comprehensive water-quality testing programme with accurate georeferencing of the well locations. A geostatistical analysis of the data can be used to quantify the spatial variability. A range of key hydrochemical parameters should be measured, not just arsenic. These should include all of the major ions, as well as iron, manganese, bicarbonate and phosphate. The study areas should not be confined to arsenic-rich areas. Parallel sediment studies should be carried out to understand the geochemical and hydrogeological processes involved. The aim is to both understand the geochemical and hydrogeological processes taking place in a quantitative way, their history and the reasons for the variability in the observed groundwater quality.

A hand-held GPS is the best way of recording the exact location of a well (along with the well owner, etc) and is now sufficiently accurate to uniquely identify the position of virtually every well in Bangladesh. At present, GPS instruments are too expensive for everyday use in Bangladesh but this will probably change with time.

Monitoring changes in arsenic concentration with time – it is important to maintain a monitoring network of wells so that any changes presently taking place can be identified. This should include wells at various depths and modes of construction, and should span the various possible timescales of change – hourly, daily, seasonal and long term. Deep wells will need monitoring less frequently than shallow wells, say every 6 months in the first instance. This should include a continuation of the present sets of piezometers constructed in this project with new sites in the low-arsenic regions. Monitoring frequency should allow a redundancy of about 50%, i.e. if you are looking for monthly changes, sample at least twice per month. This allows for some problems in sampling and analysis. The very best possible methods of chemical analysis should be used since changes are likely to be quite small. To do otherwise is a waste of time and can be misleading.

Construction of deep tubewells – it is important to ensure that there is a minimum of downward leakage of arsenic from the potentially-contaminated shallow aquifer to the deep aquifer. These may arise because of inappropriate methods of well construction, e.g. improper sealing of the shallower, contaminated horizons. Therefore methods need to be devised and promoted to ensure that wells are properly sealed when constructed. Tests should be undertaken to estimate the extent of leakage where deep wells have been

confirmed as contaminated. Natural isotopic variations and artificial tracers could prove useful for this.

Adsorption studies on Bangladesh sediments and model oxides – it is clear that adsorption-desorption processes are of critical importance in determining the extent of the groundwater arsenic problem in Bangladesh and elsewhere. Fundamental laboratory-based studies are needed to establish the quantitative nature of the arsenic adsorption isotherms and the competitive interactions that might affect the extent of arsenic adsorption in Bangladesh sediments. These should be carried out on both oxidised and reduced sediments. Speciation of solid phase iron (Fe(II), Fe(III)) and arsenic (As(III), As(V)) should be undertaken on carefully-preserved sediments. Spectroscopic methods may help to resolve this speciation at both the bulk and mineral particle scales. A detailed study of the interactions of arsenic (As(III), As(V)) and other competing solutes should be carried out on model minerals, especially iron oxides, to establish a plausible modelling approach. Possible competing anions such as phosphate, bicarbonate, silicate and dissolved organic matter should be included. This will lead to the establishment of an appropriate modelling methodology (i.e. the model itself and a database of model parameters appropriate for Bangladesh conditions).

Transport of arsenic in Bangladesh aquifers – the pathways and timescales for arsenic movement to tubewells (hand-pump and irrigation) should be established using a contaminant transport model. This should be backed up by field tracer tests and traditional hydrogeological procedures such as pump tests and piezometer monitoring. Column (laboratory) studies could be used to establish the validity of the

contaminant transport model used. The adsorption isotherm included should be consistent with the known adsorption properties of the sediments (see above). The overall aim is to be able to predict the movement of arsenic in Bangladesh aquifers under a variety of realistic hydrogeological and pumping conditions.

Impact of irrigation on the groundwater arsenic problem and the downstream impacts of using arsenic-contaminated groundwater for irrigation – although we believe that the relatively recent increase in the use of irrigation in Bangladesh is not the primary cause of the present groundwater arsenic problem, irrigation may well have some long-term impact through both hydrogeological (flow) and geochemical mechanisms. Extensive abstraction of groundwater, especially from the deeper parts of the aquifer, will alter the groundwater flow patterns within the aquifer. In general, there will be enhanced flow and mixing near the well. Given the heterogeneous distribution of arsenic within Bangladesh aquifers, this is likely to impact on the arsenic concentration in the abstracted groundwater. This needs quantifying. Large-volume urban groundwater supplies will have a similar effect.

There are also possible impacts relating to the influence of arsenic on crop growth, soil quality and the quality of any foodstuffs used for human or animal consumption.

The abstraction of groundwater for irrigation also has significant non-arsenic impacts on rural water supply in Bangladesh. The enhanced seasonal drawdown during the dry season may result in the water table falling below the depth at which traditional suction handpumps can operate. This has already happened in some parts of Bangladesh.

