## Paper 1 Arsenic occurrence in groundwater in South and East Asia

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## **Summary**

- 1. The detrimental health effects of environmental exposure to arsenic have become increasingly clear in the last few years. Drinking water constitutes one of the principal pathways of environmental arsenic exposure in humans and high concentrations found in groundwater from a number of aquifers across the world have been found responsible for health problems ranging from skin disorders to cardiovascular disease and cancer. Food represents a further potential exposure pathway to arsenic, particularly where crops are irrigated with high-arsenic groundwater or where food is cooked in high-arsenic water. However, the relative impact on human health is as yet unquantified and in need of further study.
- 2. The concentration of arsenic in natural waters globally, including groundwater, is usually low. Most have concentrations below the WHO provisional guideline value for arsenic in drinking water of  $10 \ \mu g \ L^{-1}$ . However, arsenic mobilisation in water is favoured under some specific geochemical and hydrogeological conditions and concentrations can reach two orders of magnitude higher than this in the worst cases. Most occurrences of high-arsenic groundwater are undoubtedly of natural origin.
- 3. Major alluvial and deltaic plains and inland basins composed of young sediments (Quaternary; thousands to tens of thousands of years old) are particularly prone to developing groundwater arsenic problems. Many of the identified affected aquifers are located in South and East Asia. High concentrations have been found in groundwater from such aquifers in the Bengal Basin of Bangladesh and eastern India; the Yellow River Plain and some internal basins of northern China; the lowland Terai region of Nepal; the Mekong Valley of Cambodia; the Red River delta of Vietnam; and the Irrawaddy delta of Myanmar. Problems may also emerge in similar alluvial and deltaic environments elsewhere in the world. Unfortunately, such flat-lying fertile plains are often densely populated and so poor groundwater quality can have a major impact on large numbers of people. The increasing incidence of arsenic-related health problems in these areas largely coincided with the change to using groundwater from tubewells which began in the 1970s and 1980s.
- 4. The detailed mechanisms by which the arsenic mobilisation occurs in sedimentary aquifers are still not well understood and are an area of active research. However, the development of reducing (anaerobic) conditions in the aquifers has been recognised as a key risk factor for the generation of high-arsenic groundwater. Indicators of such conditions include lack of dissolved oxygen and high dissolved iron and manganese concentrations. High-pH, oxidising (aerobic) groundwater conditions have also been linked with high groundwater arsenic concentrations in some parts of the world, though there is as yet no evidence for this means of occurrence in aquifers of South and East Asia. Arid inland basins such as occur in northern China and Mongolia represent possible areas for such conditions, but few data exist for such areas. Slow groundwater movement is also considered an important risk factor since under such conditions arsenic can be dissolved from minerals in the aquifer but is not readily flushed out of the system. Flat-lying sedimentary basins and delta plains are typically areas of such slow groundwater movement.
- 5. One of the key findings of the last few years has been that the sediments in these higharsenic aquifers do not contain unusually high arsenic concentrations. Typical concentrations are of the order of  $5-10 \text{ mg kg}^{-1}$ ; values rather close to world averages.

Nor do the sediments contain unusual arsenic minerals. It is therefore feasible that any young sedimentary aquifers could develop high-arsenic groundwater, given the special geological and hydrogeological conditions outlined above. Hence, other regions in Asia and elsewhere with young sedimentary aquifers may contain groundwater with high arsenic concentrations, but have not yet been identified. Given the increased awareness of arsenic problems and increased groundwater testing that is currently being undertaken in various parts of Asia, it is likely that other areas with problems will be identified more rapidly than was previously the case. The existence of unrecognised problems on a such a large scale as that identified in the Bengal Basin is not impossible but is considered unlikely.

- 6. Mineralised areas, particularly areas of mining activity, are also at increased risk of groundwater arsenic contamination, although unlike young sedimentary aquifers, the affected areas are typically of local extent (a few kilometres around the mineralised zone). Some geothermal areas may also give rise to increased groundwater arsenic concentrations, though this is also a less regionally significant occurrence.
- 7. Despite the advances made in recent years in understanding where high arsenic groundwaters are likely to exist on a regional scale, predictability on a local scale is still poor and probably will always be so. Short-range (well-to-well) variability in groundwater arsenic concentrations is often large. This means that individual wells used for drinking water need to be tested in recognised arsenic-affected areas. Despite common associations between arsenic and a number of other trace elements (e.g. iron, manganese) in groundwater, observed correlations in water samples are usually weak. Hence, although other elements may signal potential problems regionally, they are not reliable as proxy indicators of arsenic concentrations in individual wells.
- 8. Temporal variations in groundwater arsenic concentrations are also poorly defined. Significant seasonal and longer-term variations have been claimed to occur in some groundwaters from affected aquifers, though the information is largely anecdotal and difficult to verify. Temporal variation has major consequences for mitigation efforts and is in need of further investigation. However, in the interim, major short-term changes in groundwater arsenic concentrations are not expected in most cases. Hence, it is reasonable to assume that an initial determination is likely to be representative, provided the result is analytically reliable.
- 9. In areas affected by high-arsenic groundwater, there has been much investigation into finding alternative sources of safe (low-arsenic) drinking water. Many of the options focus on the use of surface water (including rainwater), water from dug wells and water from deep aquifers.
- 10. Surface waters usually have low dissolved arsenic concentrations. This is because of the low solid/solution ratios in surface conditions compared to aquifers, and to the oxidising conditions that pertain in most surface environments. Under oxidising conditions, adsorption of arsenic to sediments and soils occurs and mobilisation in soluble form is not favoured. Exceptions can occur locally in some mining environments as a result of direct contamination or in surface waters with a major proportion of discharging high-arsenic groundwater. However, the normally strong adsorption of arsenic to stream sediments is likely to remove the dissolved arsenic from these sources over time. Arsenic may persist in some surface waters affected by geothermal inputs or evaporation (under high-pH conditions) but high concentrations

related to these processes have not been identified in Asia and are not considered of major importance in the region. Some arsenic in surface waters may be associated with particulate matter rather than being truly dissolved, especially if the water is turbid. The overwhelming drawback of surface waters is the often poor bacterial quality. This also has major health implications and has been an important factor in determining the shift towards increased use of groundwater from tubewells in Asia over the last few decades. Surface waters therefore usually require sanitary treatment before use for potable supply.

- 11. Dug wells have also often been found to contain groundwater with low concentrations of arsenic in areas where tubewell groundwaters yield high concentrations. As with surface waters, groundwater in dug wells is typically relatively oxidising, comprising a high proportion of freshly recharged rainwater and being open to the atmosphere. Most groundwater samples analysed from dug wells in Bangladesh, West Bengal, Myanmar and Nepal have been found to contain arsenic concentrations less than 50  $\mu$ g L<sup>-1</sup> (the national standard for most countries in Asia). As a result of this, dug wells have been promoted in some high-arsenic areas as alternative sources of drinking water. However, the concentrations cannot always be guaranteed to be low. Sporadic occurrences above 50  $\mu$ g L<sup>-1</sup> have been found in groundwater from dug wells in a number of the recognised high-arsenic provinces. Some may be in the particulate rather than dissolved fraction, but such details are rarely specified in reports from the affected regions. Nevertheless, dissolved concentrations up to 560  $\mu$ g L<sup>-1</sup> have been found in dug-well water from Inner Mongolia (China) where anaerobic conditions have been maintained in low-lying areas of groundwater discharge which are characterised by sluggish groundwater movement. More chemical analysis is required to obtain an improved database of arsenic concentrations for dug wells. As with surface waters, shallow dug wells are vulnerable to contamination from surface pollutants and pathogenic organisms. They are also more prone to drying up in areas with large water-table fluctuations. They are therefore unlikely to represent a major long-term solution to the arsenic problems identified in most areas of South and East Asia, although they may provide a suitable interim solution (given adequate sanitary protection) in some affected areas if their arsenic concentrations can be demonstrated to be reliably low.
- 12. In some arsenic-affected regions of Asia, low-arsenic groundwater has been found in deeper aquifers underlying the young affected sediments. Groundwater with low arsenic concentrations ( $<10 \ \mu g \ L^{-1}$ ) has been found for example in deep aquifers in the Bengal Basin (Bangladesh, India) and the Nepal Terai. The depth at which these aquifers occurs varies considerably (tens to hundreds of metres) and so considerable confusion has arisen over the descriptions of these aquifers. The stratigraphy of the aquifers is poorly defined in most countries. More investigation has been carried out in Bangladesh than elsewhere. Here, the deep aquifers with low-arsenic groundwater are mineralogically distinct from the younger overlying sediments and are relatively oxic. They are likely to be of Pleistocene age (Quaternary; greater than 10,000 years old) and are considered to have undergone more flushing by groundwater that overlie them.
- 13. These older aquifers in Bangladesh, West Bengal and Nepal represent a potential alternative source of safe (low-arsenic) drinking water for the affected populations. However, considerable uncertainty exists over their long-term sustainability in the

event of significant exploitation. Further hydrogeological research is required to investigate whether, and to what extent, they would be susceptible to drawdown of high-arsenic groundwater from overlying aquifers or saline water in coastal areas following significant aquifer development. However, research effort on these aquifers should be complementary to the implementation of mitigation measures and not a reason for delaying them.

- 14. Although older, deeper Quaternary aquifers in the Bengal Basin and Nepal have been found to contain low groundwater arsenic concentrations, this has been found not to be the case in some other regions. In parts of northern China, high arsenic concentrations have been found in groundwater from both shallow (young Quaternary) and deeper (older Quaternary) aquifers. Here, the inland deep aquifers are thought not to have been well-flushed during the Quaternary ice ages because of slow groundwater flow and closed-basin conditions. Some groundwaters in Pleistocene aquifers of Vietnam also appear to have high arsenic concentrations. Aquifer depth is therefore not an indicator of susceptibility to arsenic mobilisation. Rather, dissolved arsenic concentrations are determined by a combination of geochemical conditions suitable for mobilising it and hydrogeological conditions which prevent its removal. Hence, groundwater quality with respect to arsenic concentrations must be considered on an aquifer-by-aquifer basis and good hydrogeological and geochemical understanding of young sedimentary aquifers is required as a prerequisite to groundwater development.
- 15. On a regional scale, our understanding of arsenic mobilisation processes is sufficiently developed to allow some kind of prediction of where arsenic problems are likely to occur and where not. Young sedimentary aquifers in alluvial and deltaic plains and inland basins are obvious areas for priority groundwater testing. Randomised reconnaissance groundwater arsenic surveys of such areas are the logical first step in identifying problem areas, followed up by more detailed surveys and mitigation if problems emerge. In identified arsenic problem areas, ideally every well used for drinking water should be tested for arsenic. Given the high toxicity of arsenic to humans, there is an argument for reconnaissance testing of groundwaters from any aquifer used for potable water supplies regardless of aquifer type and lithology. However, groundwater testing in Asia necessarily involves prioritisation with greatest emphasis on the aquifers at greatest risk.
- 16. A central tenet of both understanding the nature and scale of arsenic problems in groundwater and mitigating them is the acquisition of reliable analytical data for arsenic. Poor data can lead to erroneous conclusions and hence inappropriate responses. However, reliable chemical analysis of arsenic in water is not a trivial undertaking and requires continual attention to quality assurance. Many groundwater-arsenic analyses in Asia have been carried out using field-test kits and these are particularly prone to problems with poor precision and accuracy. Great emphasis should be placed on obtaining good-quality analytical data during testing and monitoring programmes. Such programmes need to take account of local laboratory arsenic analytical capability and build in capability development where necessary.
- 17. Although a number of groundwater provinces have been found with high arsenic concentrations, it is important to keep the scale of contamination in perspective. Groundwater from most aquifers has acceptably low arsenic concentrations and in most cases is less prone to bacterial contamination. In many areas of Asia and elsewhere, groundwater represents a reliable source of safe drinking water. Indeed, in

some arid areas, it constitutes the only source of water. Even in Bangladesh, which has suffered by far the greatest impact from groundwater arsenic problems, national statistics based on randomly collected groundwater samples indicate that 27% of shallow groundwaters (from tubewells <150 m deep) have arsenic concentrations greater than the Bangladesh standard of 50  $\mu$ g L<sup>-1</sup> and 46% have concentrations greater than 10  $\mu$ g L<sup>-1</sup>. This means that 73% and 54% respectively have concentrations below these values and are therefore deemed to be of acceptable quality. Given that considerable investment has been made in groundwater in countries such as Bangladesh over the last few decades, it would be costly and overreactive to abandon groundwater in favour of alternatives without first carrying out testing programmes and where necessary, further hydrogeological investigations.

18. This report provides an overview of the current state of knowledge on the occurrence, distribution and causes of arsenic problems in water supplies in South and East Asia. It also characterises likely 'at-risk' aquifers and the types of indicators that may be used to identify them. Response strategies in terms of analytical testing and monitoring will vary widely depending on factors such as the scale of the arsenic problem, the numbers of operating wells, the population served, the water use and the scope for alternative water sources. Some of these issues are investigated and strategies for testing and monitoring outlined.

## Introduction

## PATHWAYS OF ARSENIC EXPOSURE

The dangers associated with long-term exposure to arsenic are now well known (NRC, 1999). The most prominent health problems in affected populations are skin disorders (melanosis, keratosis, skin cancer) but a large range of other disorders including internal cancers (bladder, lung, kidney), cardiovascular diseases, peripheral vascular disorders, respiratory problems and diabetes have also been linked to chronic high doses of ingested arsenic.

Drinking water can be one of the most important pathways of exposure to arsenic in human populations and groundwater sources are thought to be responsible for the majority of the world's chronic arsenic-related health problems. Despite this, most groundwaters have low or very low concentrations of arsenic (well below regulatory and recommended limits) and in a global context they constitute often the most reliable sources of safe drinking water. Groundwater is also less vulnerable to contamination from water-borne diseases that can be a serious problem in many surface waters. It appears to be only when certain geological and hydrogeochemical conditions arise in aquifers that arsenic problems occur on a regional and problematic scale. This report describes those occurrences and the geochemical processes controlling them and attempts to provide guidance on the criteria for identifying, monitoring and dealing with these problem areas.

Although drinking water is known to be closely linked to chronic arsenic-related health problems, the sometimes poor relationship observed between arsenic intake from water and health symptoms poses the possibility that other pathways of arsenic exposure may also occur. Food is one potential source. Crops irrigated with high-arsenic groundwater are potentially vulnerable to arsenic take-up, particularly following long-term groundwater use and soil arsenic accumulation. Some studies have shown higher than background concentrations of arsenic in vegetables. Higher concentrations have typically been found in roots compared to stems, leaves or economic produce. However, few results have been published so far. Meharg and others (2003) considered that rice irrigated with high-arsenic groundwater could represent a significant contribution to the arsenic intake in some of the Bangladeshi population. In a study of dry rice grain produced by groundwater irrigation, they found concentrations up to 1.8 mg kg<sup>-1</sup> (compared for example with the 1 mg kg<sup>-1</sup> Australian standard for inorganic arsenic in food). However, few samples were analysed and the values found are higher than those in other studies of naturally cultivated rice carried out to date (Abedin and others, 2002a). The bioavailability of arsenic in rice is also uncertain and strongly influenced by the proportions of organic and inorganic forms present. Comparatively high concentrations have been found in rice straw which could affect the doses taken by grazing animals (Abedin and others, 2002b). Clearly, more research needs to be carried out on arsenic uptake by crops in irrigated areas and on food for, and produced from, grazing animals. Since arsenic is phytotoxic, uptake by vegetation may be inhibited and may therefore not be the greatest concern. However, long-term effects on crop yield, especially rice, could become an important issue (Abedin and Meharg, 2002).

Arsenic-contaminated air is also a potential exposure pathway in some cases. In Guizou Province of southern China, severe chronic health problems have arisen from the burning of local coal with very high arsenic concentrations (up to  $35,000 \text{ mg kg}^{-1}$ ), the exposure being both by inhalation and consumption of chillis dried over domestic coal fires (Finkelman and others, 1999). This pathway is much more localised than that from drinking water but in China, an estimated 3000 people in several villages of Guizhou Province have arsenicosis symptoms as a result of exposure from this source (Ding and others, 2001).

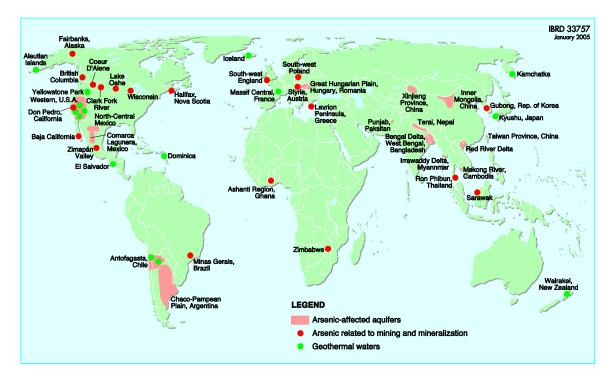
#### **DRINKING-WATER REGULATIONS AND GUIDELINES**

Regulatory and recommended limits for arsenic in drinking water have reduced in recent years following increased evidence of its toxic effects to humans. The World Health Organization (WHO) guideline value reduced from  $50 \ \mu g \ L^{-1}$  to  $10 \ \mu g \ L^{-1}$  in 1993 although the recommendation is still provisional pending further scientific evidence (WHO, 1993). Western countries are reducing, or have reduced, their national standards in line with this change. Despite this, national standards for arsenic in most Asian countries (except Japan) remain at  $50 \ \mu g \ L^{-1}$  in line with the pre-1993 WHO guideline value. This is largely a consequence of analytical constraints and in some countries of difficulties with compliance to a lower standard.

### WORLD DISTRIBUTION OF HIGH-ARSENIC GROUNDWATERS

The concentrations of arsenic in most groundwaters are low, typically being less than the WHO guideline value of 10  $\mu$ g L<sup>-1</sup> and commonly below analytical detection limits. An investigation of some 17,500 groundwater samples from public-supply wells in the USA for example found that 7.6% exceeded 10  $\mu$ g L<sup>-1</sup> and 1% exceeded 50  $\mu$ g L<sup>-1</sup> while 64% contained <1  $\mu$ g L<sup>-1</sup> (Focazio and others, 1999). Despite the usually low abundance in water, high concentrations can occur in some groundwaters. Under geochemically and hydrogeologically favourable conditions, concentrations can reach tens to hundreds of  $\mu$ g L<sup>-1</sup> and in a few cases, in excess of 1 mg L<sup>-1</sup>.

Most of the world's high-arsenic groundwater provinces result from natural processes involving interactions between water and rocks. Some of the highest concentrations of arsenic are found in sulphide and oxide minerals, especially iron sulphides and iron oxides (Smedley and Kinniburgh, 2002). As a result, high arsenic concentrations in water are often found where these minerals are in abundance. Mineralised areas are well-documented examples. These contain ore minerals, including sulphide minerals, typically as veins or replacements of



**Figure 1.** Summary of the world distribution of documented problems with arsenic in groundwater and the environment (after Smedley and Kinniburgh 2002).

original host rocks and result from past infiltration of hydrothermal fluids. In mineralised areas, rates of mineral dissolution can be enhanced significantly by mining activity and arsenic contamination can be particularly severe in water associated with mine wastes and mine drainage. Some geothermal waters also contain high arsenic concentrations.

A map of the distribution of documented cases of arsenic contamination in groundwater and the environment is given in Figure 1. Many of these cases are related to areas of mineralisation and mining activity and a few are associated with geothermal sources. While these cases can be severe with often high concentrations of arsenic in waters, sediments and soils, the contamination is usually not of large lateral extent. This results from the normally strong adsorption capacity of iron oxides that leads to removal of arsenic and other potentially toxic trace elements from water.

Despite these associations, other areas with recognised high-arsenic groundwaters are not associated with obvious mineralisation or geothermal activity. Some of these occur in major aquifers and may be potentially much more serious because they occupy large areas and can provide drinking water for large populations. Unlike mining and geothermal areas, they are also more difficult to detect without chemical analysis of the groundwater. Several aquifers around the world have now been identified with unacceptably high concentrations of arsenic. These include aquifers in parts of Argentina, Chile, Mexico, south-west USA, Hungary, Romania, Bangladesh, India, China, Myanmar, Nepal, Taiwan and Vietnam (Figure 1). Many differences exist between these regions, but some similarities are also apparent. The majority of the high-arsenic groundwater provinces are in young unconsolidated sediments, usually of Quaternary age, and often of Holocene (<12,000 years) age. These aquifers are usually large inland closed basins in arid or semi-arid settings (e.g. Argentina, Mexico, south-west USA) or large alluvial and deltaic plains (e.g. Bengal delta, Yellow River Plain, Irrawaddy delta, Red River delta). These aquifers do not appear to contain abnormally high concentrations of arsenic-bearing minerals but do have geochemical and hydrogeological conditions favourable for mobilisation and retention in solution.

# Arsenic distribution in South and East Asia

## **OVERVIEW**

Many of the world's aquifers with recognised arsenic problems are located in Asia, where large alluvial and deltaic plains occur, particularly around the perimeter of the Himalayan mountain range. This section gives an account of the occurrence and scale of groundwater arsenic problems in countries where such problems have been identified. There may be other Quaternary aquifers with high groundwater arsenic concentrations that have not yet been identified, but since awareness of the arsenic problem has grown substantially over the last few years, these are likely to be on a smaller scale than those already identified.

The information in this section has been compiled from published literature, as well as various unpublished reports and websites. Many of the unpublished data are difficult to access and reports typically not peer reviewed. Data for many countries also lack spatial information, particularly georeferenced sample points. Reporting often merely gives an indication of whether an area is or is not affected, rather than an account of percentages of affected wells in a given area. In some cases, the quality of analytical data is also uncertain (Box 1). These uncertainties make it difficult to assess the scale of arsenic problems in many parts of South and East Asia. Nonetheless, the information available has been brought together to provide a critical assessment of the current state of knowledge of the scale of groundwater contamination of the aquifers in Asia and to detail where apparent data gaps exist. A summary of the recognised occurrences, aquifers involved and populations potentially at risk (i.e. using drinking water with arsenic concentrations >50  $\mu$ g L<sup>-1</sup>) is given in Table 1. Some of these population statistics are poorly constrained given the present state of knowledge.

## ALLUVIAL, DELTAIC AND LACUSTRINE PLAINS

## Bangladesh

Of the regions of the world with groundwater arsenic problems, Bangladesh is the worst case

Location	Areal extent (km <sup>2</sup> )	Population at risk <sup>a</sup>	As range $(\mu g L^{-1})$		
Alluvial/deltaic/lacustrine plains					
Bangladesh	150,000	35 million	<1-2300		
China (Inner Mongolia,	68,000	5.6 million	40-4400		
Xinjiang, Shanxi)					
India (West Bengal)	23,000	5 million	<10-3200		
Nepal	30,000	550,000	<10-200		
Taiwan	6000	? 10,000 <sup>b</sup>	10-1800		
Vietnam	1000	10 million <sup>c</sup>	1-3100		
Myanmar	?3000	3.4 million	-		
Cambodia	?<1000	320,000 <sup>d</sup>	-		
Pakistan	-	-	-		
Mineralised areas					
Thailand	100	15,000	1-5000		

**Table 1**. Summary of the distribution, nature and scale of documented arsenic problems (>50  $\mu$ g L<sup>-1</sup>) in aquifers in South and East Asia.

not available

<sup>a</sup>Estimated to be drinking water with arsenic >50  $\mu$ g L<sup>-1</sup>. From Smedley (2003) and data sources therein <sup>b</sup>before mitigation

<sup>°</sup>UNICEF estimate

<sup>d</sup>Maximum

#### Box 1. Analysis of arsenic

Arsenic is a trace element that is present at  $\mu g L^{-1}$  concentrations in most natural waters. Sampling and analysing such small concentrations is not a trivial task and there have been many examples in recent years where faulty analysis has led to dubious conclusions. All surveys require a planned and maintained quality-assurance (QA) programme to ensure data produced are of good quality throughout the programme. This includes adequate record keeping, sample tracking, regular use of analytical standards, inter-laboratory (round-robin) checks and duplicate analyses.

The most precise and sensitive analytical methods depend on sophisticated laboratory instruments such as hydride generation-atomic absorption spectrophotometry (HG-AAS), inductively coupled plasma-mass spectrometry (ICP-MS) and HG-atomic fluorescence spectrometry (HG-AFS). The use of HG-AAS has expanded in recent years, but many developing countries do not have such sophisticated facilities or have difficulty maintaining them, especially on the scale required. Costs of analysis by these techniques are typically in the range \$10-20 per sample. The HG-AAS and HG-AFS methods are at the cheaper end of this range, but the more expensive ICP methods are multi-element techniques and so provide more information than just arsenic. There are cheaper and more robust instruments such as that employed by the 'SDDC method' but these are less sensitive, are slow and may not be appropriate for large screening programmes. Field-test kits have therefore been widely used as a primary source of data in many surveys, with laboratory methods used for checking some of the results. Field-test kits are relatively simple and inexpensive, usually costing less than \$1 per sample for the materials. The early kits were insufficiently sensitive (being barely capable of detecting less than 100  $\mu$ g L<sup>-1</sup>). However, they have improved in the last few years and the best can now detect down to 10  $\mu$ g L<sup>-1</sup>, the WHO guideline value. In practice, the accuracy and reproducibility of the kits has often proved disappointing (Rahman and others, 2002) and care has to be taken to ensure that good results are obtained consistently during a survey.

As a result of the relatively large errors involved in arsenic analysis, especially with field-test kits, it is inevitable that some wells will be misclassified as 'safe' when they are not, and vice versa. Procedures should be in place to assess the scale and significance of these misclassifications and to minimise their impact, e.g. by reanalysing samples that are very different from those taken from neighbouring wells. The reliability of the kits increases for concentrations well above the drinking-water standard or guideline and so they tend to be more reliable at detecting the most toxic waters.

identified, with some 35 million people thought to be drinking groundwater containing arsenic at concentrations greater than 50  $\mu$ g L<sup>-1</sup> (Table 1) and around 57 millions drinking water with concentrations more than 10  $\mu$ g L<sup>-1</sup> (Gaus and others, 2003). The large scale of the problem reflects the large area of affected aquifers, the high dependence of Bangladeshis on groundwater for potable supply and the large population in the fertile lowlands of the Bengal Basin. Today, there are an estimated 11 million tubewells in Bangladesh serving a population of around 133 million people (2002 estimate). The scale of arsenic contamination in Bangladesh means that it has received by far the greatest attention in terms of groundwater testing and more is known about the arsenic distribution in the aquifers than in any other country in Asia (as well as most of the developed world). However, much more testing is still required.

Several surveys of arsenic in Bangladesh groundwater have been carried out over the last few years, both by laboratory and field methods. DPHE/UNICEF carried out surveys of 51,000 wells during 1997–1999 using arsenic field-test kits. BGS and DPHE conducted a survey of around 3500 samples nationwide during 1998-1999 (BGS and DPHE, 2001). Over the last few years, BAMWSP and a number of NGOs and international agencies (e.g. JICA, AAN,

NGO Forum, UNICEF, World Vision International, Watsan Partnership) have carried out major screening programmes of groundwaters across Bangladesh. Van Geen and others (2003b) also analysed samples from about 6000 wells in eastern Bangladesh. To date more than 1 million tubewells have been tested for arsenic. However, this is still only around 10% of the wells in the country.

#### HIGH-ARSENIC SHALLOW AQUIFERS

The aquifers affected by arsenic are Quaternary, largely Holocene, alluvial and deltaic sediments associated with the Ganges-Brahmaputra-Meghna river system. These occur as the surface cover over a large part of Bangladesh. Groundwater from the Holocene aquifers contains arsenic at concentrations up to around 2300  $\mu$ g L<sup>-1</sup>, though concentrations span more than four orders of magnitude (BGS and DPHE, 2001). Van Geen and others (2003b) found concentrations in the range <5–860  $\mu$ g L<sup>-1</sup> in groundwaters from Araihazar, east of Dhaka.

Several surveys of the groundwater have shown a highly variable distribution of arsenic, both laterally and with depth. This means that predictability of arsenic concentrations in individual wells is poor and each well used for drinking water needs to be tested. Nonetheless on a regional scale, trends are apparent and the worst-affected areas with the highest average arsenic concentrations are found in the south-east of the country, to the south of Dhaka (Figure 3). Here in some districts, more than 90% of shallow tubewells tested had arsenic concentrations >50  $\mu$ g L<sup>-1</sup>.

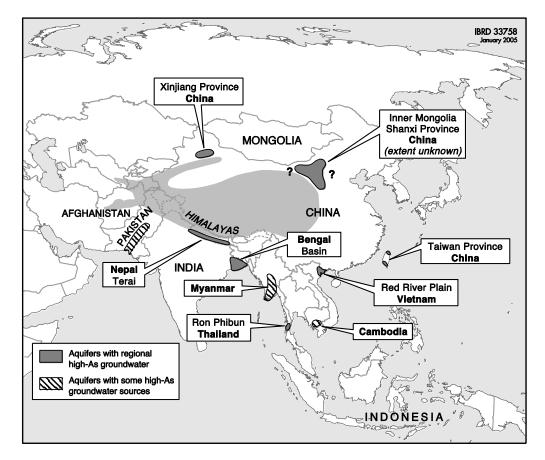


Figure 2. Map of South and East Asia showing the locations of documented high-arsenic groundwater provinces.

Tubewell depth range (m)*	Number of samples (%)			Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50 \ \mu g \ L^{-1}$	
<25	597 (53)	193 (17)	327 (30)	1117
25-50	740 (57)	211 (16)	354 (27)	1305
50-100	363 (55)	143 (22)	153 (23)	659
100-150	33 (26)	47 (37)	46 (37)	126
150-200	25 (78)	6 (19)	1 (3)	32
>200	286 (97)	7 (2)	2(1)	295

**Table 2.** Frequency distribution of arsenic in groundwater from tubewells from Quaternary alluvial aquifers in Bangladesh (from BGS and DPHE, 2001).

\*Depth of intake of groundwater is difficult to determine and may be from several horizons at differing depths.

Some areas with low overall arsenic concentrations have localised 'hotspots' with locally high arsenic concentrations. That of the Chapai Nawabganj area of western Bangladesh is a notable example (Figure 4), where the median concentration in groundwater from Holocene sediments was found to be  $3.9 \ \mu g \ L^{-1}$  but with extremes up to  $2300 \ \mu g \ L^{-1}$  concentrated in a small area of around 5 x 3 km. Overall, the BGS and DPHE survey of shallow groundwaters found that 27% exceeded 50  $\ \mu g \ L^{-1}$  and 46% exceeded 10  $\ \mu g \ L^{-1}$ .

Investigation of the depth ranges of affected tubewells suggests that concentrations are low in groundwater from the top few metres of the aquifers close to the water table, but that they increase markedly over a short depth range. This is demonstrated by the profile of

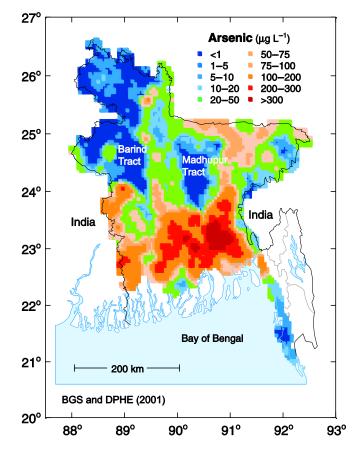


Figure 3. Smoothed map of arsenic distribution in groundwater from Bangladesh (from BGS and DPHE, 2001). Samples included are from tubewells <150 m deep.

**Box 2.** Shallow versus deep aquifers

It has been observed that groundwater from deep Quaternary aquifers in the Bengal Basin (Bangladesh and West Bengal) has low or very low concentrations of arsenic, often much less than  $5 \ \mu g \ L^{-1}$ . The depth at which these deep aquifers occurs varies but is typically more than 100–150 m below surface. Deep aquifers have been tapped in southern coastal areas and north-eastern Bangladesh for some time but less so in other areas and their stratigraphy, lithology and areal extent are often poorly defined. They are often said to be more 'oxic' than the younger overlying deposits with a higher proportion of brown iron oxides. As older formations, they are also likely to have been better flushed by groundwater than the overlying young sediments as a result of enhanced groundwater gradients and more active water movement during past ice ages. As sources of low-arsenic groundwater, these deep aquifers could provide drinking water for affected populations in the region. More research is needed however, to establish whether they would be secure from the effects of downward leakage of high-arsenic water (or saline water in coastal areas) given significantly increased groundwater abstraction.

In other regions of South and East Asia, groundwater from deep Quaternary aquifers does not always have low arsenic concentrations. In Inner Mongolia, concentrations of arsenic up to  $310 \ \mu g \ L^{-1}$  have been found in groundwater from wells more than 100 m deep in an area where a shallow aquifer (less than 30 m deep) also has high groundwater arsenic concentrations. The lithology and stratigraphy of the deep aquifer are poorly characterised. However, it is clear from the comparisons that groundwater arsenic concentration is not a simple function of aquifer or well depth. Rather, aquifer geology and groundwater flow history are important controlling factors. Observations show that a good understanding of the hydrogeology and geochemistry of Quaternary alluvial, deltaic and lacustrine aquifers is needed before significant groundwater development should be allowed to take place.

groundwater compositions in a piezometer (10 cm diameter, 40 m deep) in Chapai Nawabganj, north-west Bangladesh. Arsenic concentration was relatively low (17  $\mu$ g L<sup>-1</sup>) at 10 m depth but increased to values in the range 330–400  $\mu$ g L<sup>-1</sup> over the depth interval 20–40 m (BGS and DPHE, 2001) (Figure 5).

The largest range and highest concentrations of arsenic are typically found at around 15–30 m depth below surface, although the depth ranges of the peaks vary from place to place. Table 2 shows the frequency distribution of arsenic concentrations with depth for all analysed samples from the BGS and DPHE (2001) survey.

Investigation of other elements of potential health concern reveals that concentrations of manganese are often greater than the WHO health-based guideline value of  $0.5 \text{ mg L}^{-1}$  and concentrations of uranium are also sometimes high (up to  $32 \mu g L^{-1}$ ). Concentrations of boron exceed WHO guidelines in some saline groundwaters from the south and east of Bangladesh. Nitrate concentrations are normally low, as are most other trace elements on the WHO list of elements considered detrimental to health. Concentrations of iron and ammonium are often high but these are more issues of acceptability on aesthetic grounds rather than health considerations.

#### LOW-ARSENIC AQUIFERS

The BGS and DPHE (2001) map (Figure 3) demonstrates the low overall arsenic concentrations of groundwater from coarser sediments in the Tista Fan of northern Bangladesh. Low concentrations are also found in groundwaters from aquifers in the older (Pleistocene) uplifted plateaux of the Barind and Madhupur Tracts (north-central Bangladesh). These usually have concentrations less than 10  $\mu$ g L<sup>-1</sup> and often significantly

less. Similar results for these areas have also been obtained by other workers (e.g. van Geen and others, 2003b). Groundwater from these areas is therefore expected to be normally safe from the point of view of arsenic, although concentrations of other elements, notably iron and manganese, may be high.

Arsenic concentrations also appear to be mostly low in groundwater from older ('deep') aquifers which occur in some areas below the Holocene deposits. The stratigraphy of the deep aquifers of Bangladesh is poorly understood at present, but where studied, the aquifers with low-arsenic groundwater appear to be of Pleistocene age (BGS and DPHE, 2001; van Geen and others, 2003b). Limited investigations indicate that they are mineralogically distinct from the overlying Holocene deposits. They are typically more brown in colour and relatively oxidised. The deep aquifer sediments are likely to be akin to the aquifers below the Barind and Madhupur Tracts which occur at shallower depths by virtue of tectonic uplift.

Although these sediments are often referred to as the 'deep aquifer', the definition of 'deep' varies from place to place and between organisations and the subject has become rather confused (Box 2). However, depth ranges for the low-arsenic groundwater are usually at least 100–200 m. Recent data produced by BAMWSP for groundwater samples from 60 upazilas across Bangladesh found that out of 7123 samples from tubewells >150 m deep, 97% had arsenic concentrations  $<50 \ \mu g \ L^{-1}$  (percentage  $<10 \ \mu g \ L^{-1}$  unspecified; BAMWSP website). The BGS and DPHE (2001) national survey categorised 'shallow' aquifers as those less than 150 m depth and 'deep' as greater than 150 m. Of 335 samples analysed from >150 m depth, 95% were found to have arsenic concentrations  $<10 \ \mu g \ L^{-1}$  (Table 2). Most of the deep groundwater samples analysed in the BGS and DPHE survey were from the southern coastal area (Barisal) and the north-east (Sylhet). In these areas, the shallow and deep aquifers appear to be separated by thick deposits of clay which afford some hydraulic separation between the two. By contrast, in a local study of groundwater in Faridpur area of central Bangladesh, BGS

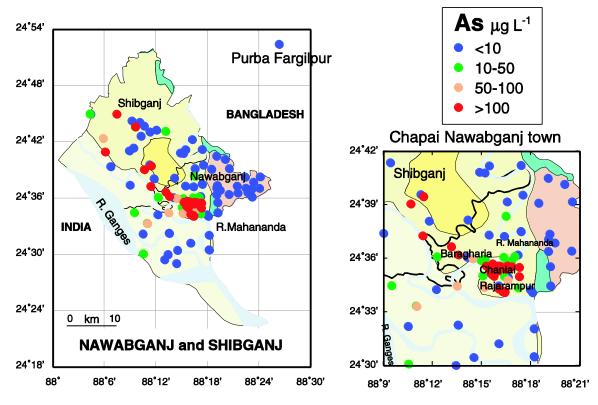


Figure 4. Maps of the distribution of arsenic in shallow groundwater from the Chapai Nawabganj area, north-west Bangladesh (from BGS and DPHE, 2001).

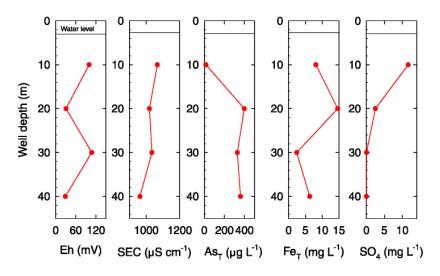
and DPHE (2001) defined the deep aquifer as being greater than 100 m, based on the occurrence of sandy sediments and well depths. Here the deeper aquifer was found not to be well-separated from the shallower aquifer and a degree of hydraulic connection between the two is therefore possible (BGS and DPHE, 2001). Chemical analysis of samples from Faridpur revealed arsenic concentrations up to 52  $\mu$ g L<sup>-1</sup> (5 samples) in groundwater from >100 m depth. Closer investigation of the wells with higher concentrations also showed that they were sometimes screened at multiple levels and hence took in water from various horizons.

Van Geen and others (2003b) also found consistently lower arsenic concentrations at greater depth in the Araihazar area east of Dhaka. Here the low concentrations were found at depths as shallow as 30 m, although the range of the low-arsenic 'deep' aquifer varied between 30 m and 120 m. There is some question over whether the 'deep' aquifer at 30 m results from uplift of the sediments, as the study area is on the eastern edge of the Madhupur Tract.

The results clearly indicate that the depth of 'safe' aquifers (from an arsenic point of view) varies in different parts of Bangladesh and it is not possible to define the depth at which lowarsenic water will occur, even assuming a deep aquifer exists in all areas. The variable depths are perhaps not surprising given the heterogeneity of sediments in the basin and complexities introduced by past tectonic movements. The important criterion for determining the groundwater arsenic concentrations is the sediment type and sediment history rather than depth.

From available data, it also appears that concentrations of manganese and uranium are lower in the groundwater from the deeper aquifer (BGS and DPHE, 2001). Concentrations of most other analysed trace elements were also within acceptable ranges.

Although a number of studies have been and are being carried out on the Bangladesh deep aquifers, much remains unknown about their distribution across the country, the degree of hydraulic separation from the shallow high-arsenic aquifers and their viability as a long-term source of water. Questions also remain about why higher arsenic concentrations occur in some samples. Possibilities include drawdown from shallow levels due to hydraulic connection, drawdown via wells due to poor sealing, multiple screening of wells in both aquifers or in-situ high-arsenic groundwater in some parts of the deep aquifer. These questions are critical to the future potential of the deep aquifers for water supply and need



**Figure 5.** Variation in concentration of arsenic and other elements with depth in a purpose-drilled piezometer in Chapai Nawabganj, north-west Bangladesh (from BGS and DPHE, 2001).

#### Box 3. Dug wells

Concentrations of arsenic in dug wells are often low, even in areas where those in groundwater from neighbouring tubewells are high. In western Bangladesh, a 30 m deep tubewell with a groundwater arsenic concentration of around 2300  $\mu$ g L<sup>-1</sup> is located just a few metres from an 8 m deep dug well with an arsenic concentration of less than 4  $\mu$ g L<sup>-1</sup>. Groundwater in the top few metres below the water table is likely to be relatively aerobic because of recent inputs of rainfall and more active groundwater movement. However, it is most likely that the tendency for low arsenic concentrations in dug wells relates in large part to their large diameter and openness to atmosphere compared to tubewells.

Despite the tendency for low arsenic concentrations in dug-well waters, not all are found to be below acceptable limits. Several dug wells from the Bengal Basin have been found with concentrations greater than the WHO guideline value of  $10 \ \mu g \ L^{-1}$ . Worse, in parts of Inner Mongolia where tubewell water has high concentrations, groundwater from dug wells has been found with concentrations up to 560  $\ \mu g \ L^{-1}$ . The concentration of arsenic in dug wells is probably largely controlled by the redox conditions in the wells; where anaerobic conditions can be maintained, arsenic concentrations may be unacceptably high. Concentrations may also be high where locally influenced by mining wastes. The concentrations of arsenic in dug wells can therefore not always be guaranteed to be low, and testing for arsenic needs to be carried out to assess their safety for potable purposes.

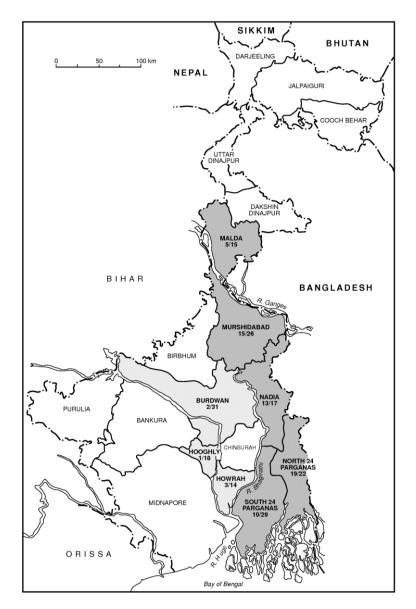
Additional problems from dug wells occur because of their shallow depths. They can be at increased risk from contamination by surface pollutants, including pathogenic bacteria, and will generally require disinfection before use. Enclosure of the well and adding a hand-pump may also be necessary. Restricted yields and seasonal drying up of wells are additional problems affecting their usefulness in some areas.

In many parts of South and East Asia, dug wells have been superseded over time by hand-pumped tubewells as a means of obtaining improved yields and sanitary protection. Nonetheless, they are still used by significant numbers of people, and their use in some areas has increased where they provide an alternative to high-arsenic tubewell water. In Bangladesh, around 1.3 million people are estimated to be dependent on dug wells for drinking water (Ahmed and Ahmed, 2002), though not all of these draw water from the unconsolidated sediments of the Bengal Basin.

further assessment before development of these aquifers takes place on a large scale.

#### DUG WELLS

A number of studies have concluded that arsenic concentrations in shallow dug wells in Bangladesh are usually low, even in areas where tubewells have high concentrations (Box 3). Concentrations are generally  $<50 \ \mu g \ L^{-1}$ , with most being  $<10 \ \mu g \ L^{-1}$  (e.g. Chakraborti, 2001). BGS and DPHE (2001) found concentrations in five dug wells from north-west Bangladesh (Chapai Nawabganj) in the range  $<3-14 \ \mu g \ L^{-1}$  with a median of 7.6  $\mu g \ L^{-1}$ . Two samples exceeded 10  $\mu g \ L^{-1}$ , albeit by a small margin. However, these were from an area with lower overall groundwater arsenic concentrations than the worst-affected parts of the country. Little difference was observed in the samples between concentrations in filtered and unfiltered aliquots and the concentrations were therefore considered to be largely dissolved. Concentrations of uranium up to 47  $\mu g \ L^{-1}$ , manganese up to 1.7 mg \ L^{-1} and nitrate-N up to 28 mg \ L^{-1} were found in the dug wells from the region, all of which exceed current WHO health-based guideline values. Bacterial counts in dug wells are also often high.



**Figure 6.** Map of West Bengal showing districts affected by high groundwater arsenic concentrations. Numbers refer to number of blocks with arsenic concentrations  $>50 \ \mu g \ L^{-1}$  relative to total number of blocks. Darker shading shows worst-affected areas (data as of 1999).

#### Bengal delta and associated aquifers, India

Problems with arsenic in groundwater in West Bengal were first recognised in the early 1980s and the health effects are now reasonably well documented. Today, it is estimated that more than 5 million people in the state are drinking water with arsenic concentrations greater than 50  $\mu$ g L<sup>-1</sup> (). More recently, problems have also been found in Bihar, Tripura and Uttar Pradesh. The states of Assam, Meghalaya and Mizoram also have important Quaternary sedimentary aquifers which are potentially at risk from high groundwater arsenic concentrations. Recent findings of health problems in the village of Semria Ojha Patti in Bihar prompted a survey of groundwater arsenic concentrations. Of 206 tubewells tested, 57% exceeded 50  $\mu$ g L<sup>-1</sup> and 20% exceeded 300  $\mu$ g L<sup>-1</sup>. Concentrations were up to 1650  $\mu$ g L<sup>-1</sup> (Chakraborti and others, 2003). Associated health problems are also severe, with skin lesions reported to be prevalent in 13% of adults and 6.3% of children and neurological problems in 63% of adults. As the water samples were collected from villages with identified health

problems, the concentrations represent worst cases and the statistics are unlikely to be representative of the arsenic concentrations in the state as a whole.

More than 100,000 groundwater arsenic analyses have apparently been determined for West Bengal. Despite this, there still appears to be a lack of detailed maps of arsenic to assess the spatial distribution. Worst-affected districts have been identified but the distributions on a larger scale (within districts) are not clear and it is thought that no point-source maps of groundwater arsenic concentrations have been produced. The scale of the problems in other states with similar geology (Tripura, Bihar, Uttar Pradesh, Meghalaya, Mizoram) is also not known.

The affected aquifers of the region are mainly Holocene alluvial and deltaic sediments similar to those of large parts of Bangladesh. In West Bengal, they form the western margins of the Bengal Basin. High arsenic concentrations have been identified in groundwaters from some tubewells in up to eight districts of West Bengal, the five worst-affected being Malda, Murshidabad, Nadia, 24 North Parganas and 24 South Parganas (Figure 6). These cover around 23,000 km<sup>2</sup>, to the east of the Bhagirathi-Hoogli river system. Arsenic concentrations have been found in the range  $<10-3200 \ \mu g \ L^{-1}$  (Table 1; CGWB, 1999). At the time of writing, no data on arsenic concentrations in groundwater from Chinsurah district are available. Groundwaters from the laterite upland in the western part of West Bengal, as well as the Barind and Ilambazar Formations, the valley margin fan west of the Bhagirathi river and the lower delta plain and delta front have low groundwater arsenic concentrations (PHED, 1991).

The Quaternary sediment sequence increases in thickness southwards (CGWB, 1999). Sedimentation patterns vary significantly laterally, but sands generally predominate to a depth of 150–200 m in Nadia and Murshidabad while the proportion of clay increases southwards into 24 North and South Parganas, as does the thickness of surface clay (Ray, 1997).

The Quaternary sediments have a similar configuration to those of Bangladesh but the aquifers have been categorised slightly differently. A shallow 'first aquifer' has been described at 12–15 m depth, with an intermediate 'second aquifer' at 35–46 m and a deep 'third aquifer' at around 70–90 m depth (PHED, 1991). High arsenic concentrations occur in groundwater from the intermediate 'second aquifer'. Shallowest groundwaters ('first aquifer') appear to have low concentrations, presumably because many (though not necessarily all) of the sources abstracting from this depth are open dug wells and are likely to contain groundwater which is oxidised through exposure to the atmosphere. Groundwaters from the deep aquifer also have low arsenic concentrations, except where only a thin clay layer separates it from the overlying aquifer, allowing some hydraulic connection between them. CGWB (1999) noted that the depths of arsenic-rich groundwaters vary in the different districts but that where high-arsenic groundwaters exist, they are generally in the depth range of 10–80 m. As with Bangladesh therefore, the groundwater arsenic concentration ranges appear to show a bell-shaped curve with depth.

As with Bangladesh, the distribution of arsenic concentrations in the groundwaters is known to be highly variable. Some particularly high concentrations (>200  $\mu$ g L<sup>-1</sup>) have been found in groundwaters from 24 South Parganas, along the international border of 24 North Parganas and in eastern Murshidabad (Acharyya, 1997; CSME, 1997).

## Terai region, Nepal

Groundwater is abundant in the Quaternary alluvial sediments of the lowland Terai region of southern Nepal and is an important resource for domestic and agricultural use. The region is estimated to have around 200,000 tubewells which supply groundwater for some 11 million

Agency	Nu	mber of samples (%)		Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50 \ \mu g \ L^{-1}$	-
DWSS	3479 (89.3)	289 (7.3)	128 (3.3)	3896
NRCS	2206 (79)	507 (18)	77 (3)	2790
Finnida	55 (71)	14 (18)	9 (12)	78
Tandukar	54 (61)	27 (30)	8 (9)	89
NASC (2003 data)	17300 (69)	6000 (23)	2000 (8)	25000

**Table 3.** Frequency distribution of arsenic concentrations in analysed groundwater samples from Nepal<br/>(Chitrakar and Neku, 2001; Tandukar, 2001; Neku and Tandukar, 2003).

people (Chitrakar and Neku, 2001). About 50% of these wells were supplied by government agencies or NGOs, the rest being private wells. Many have been installed within the last decade. Groundwater is also used for irrigation; these wells generally abstracting from deeper levels than those used for drinking water.

Both shallow and deep aquifers occur throughout most of the Terai region, although the thickness of sediments deposited is significantly less than found in Bangladesh. The shallow aquifer appears to be mostly unconfined and well-developed, although it is thin or absent in some areas (Upadhyay, 1993). The deep aquifer (precise depth uncertain) is artesian. Quaternary alluvium also infills several intermontaine basins in Nepal, most notably that of the Kathmandu Valley of central Nepal (ca. 500 km<sup>2</sup>) where sediment thickness reaches in excess of 300 m (Khadka, 1993). Recent heavy abstraction of groundwater in the Kathmandu Valley has resulted in falling groundwater levels (Tuinhof and Nanni, 2003).

A number of surveys of groundwater quality in the Terai region have revealed the presence of arsenic at high concentrations in some shallow tubewells (<50 m depth), though most of those analysed appear to have <10  $\mu$ g L<sup>-1</sup>. Arsenic-related health problems have been detected in some of the affected areas. Water analyses have mostly been determined (by HG-AAS) by four private laboratories in Nepal with additional analyses from four government laboratories (Tuinhof and Nanni, 2003).

The most recent water-quality statistics have been compiled by the National Arsenic Steering Committee (NASC), set up in 2001 to oversee and coordinate national arsenic testing and mitigation (Neku and Tandukar, 2003; Tuinhof and Nanni, 2003; Shrestha and others, 2004). As of September 2003, some 25,000 water analyses of arsenic had been carried out and results indicate that 69% of groundwaters sampled had arsenic concentrations less than 10  $\mu$ g L<sup>-1</sup>, while 31% exceeded 10  $\mu$ g L<sup>-1</sup> and 8% exceeded 50  $\mu$ g L<sup>-1</sup> (Tuinhof and Nanni, 2003; Shrestha and others, 2004). Worst affected were the districts of Rautahat, Bara, Parsa, Kapilbastu, Nawalparasi, Rupandehi, Banke, Kanchanpur and Kailali of the central and western Terai. The highest concentration observed (Rupandehi district) is 2600  $\mu$ g L<sup>-1</sup> (Shrestha and others, 2004).

Results from earlier surveys (Table 3) show similar overall statistics to the more recent summary. The Nepal Department of Water Supply and Sewerage (DWSS) carried out a survey of some 4000 tubewells from the 20 Terai districts, mostly analysed by field-test kits but with laboratory replication of some analyses. Results from the survey indicated that 3.3% of the samples had arsenic concentrations of >50  $\mu$ g L<sup>-1</sup> (Chitrakar and Neku, 2001). The highest observed concentration was 343  $\mu$ g L<sup>-1</sup> (Parsa District). From testing in 17 of the 20 Terai districts, the Nepal Red Cross Society (NRCS), also found 3% of groundwater sources sampled having concentrations above 50  $\mu$ g L<sup>-1</sup>, the highest observed concentration being 205  $\mu$ g L<sup>-1</sup>. The spatial distribution of the worst-affected areas was found to be similar to that reported by Chitrakar and Neku (2001). A Finnida survey found 12% of analysed samples exceeding 50  $\mu$ g L<sup>-1</sup> while a survey by Tandukar found 9% of samples exceeding this value

(Table 3). The highest arsenic concentrations observed by Tandukar (2001) were around 120  $\mu$ g L<sup>-1</sup>, most of the high-arsenic samples being from the River Bagmati area. The high arsenic concentrations occur in anaerobic groundwaters and are often associated with high concentrations of dissolved iron (Tandukar, 2001). The percentage of samples with exceedances above 50  $\mu$ g L<sup>-1</sup> is generally small and much lower than observed in Bangladesh for example, but the statistics nonetheless indicate a clear requirement for further testing and remedial action. To date, there has been no substantial mitigation programme in the region (Tuinhof and Nanni, 2003).

Surveys appear to indicate that deeper tubewells in the Terai have lower arsenic concentrations. As with Bangladesh, variation in arsenic concentration with depth appears to show a general bell-shaped curve. The largest variation and highest maximum concentrations occur in tubewells with depths in the 10–30 m range. Concentrations are generally  $<50 \ \mu g \ L^{-1}$  at depths greater than around 50 m (Shrestha and others, 2004). Recent analysis of groundwater from 522 irrigation wells, with depths of >40-50 m, were also found to have low concentrations (Tuinhof and Nanni, 2003). This suggests that the deep aquifer offers some possibilities as an alternative source of low-arsenic water supply. However, as with Bangladesh, the susceptibility of groundwater from the deep aquifer to drawdown of high-arsenic water from overlying sediments is a matter for concern and further hydrogeological investigation.

At the time of writing, around 13% of wells thought to exist in the Terai region have been tested for arsenic. Data so far available from the Kathmandu Valley have revealed no arsenic problems there, although the extent of testing in the valley is not clear.

### Irrawaddy delta, Myanmar

As elsewhere in Asia, traditional sources of water for domestic supply in Myanmar were dug wells, ponds, springs and rivers. However in the Quaternary aquifer of the Irrawaddy delta, many of these have been superseded since 1990 by the development of shallow tubewells. It is estimated that more than 400,000 wells exist in Myanmar as a whole, more than 70% of which are privately owned (UNICEF, 2002). Little testing for arsenic in groundwater has been carried out in tubewells from the alluvial aquifer. However a few reconnaissance surveys have been undertaken and arsenic has been found in excess of 50  $\mu$ g L<sup>-1</sup> in some. Save The Children reported from analysis of 1912 shallow tubewells in four townships in Avevarwaddy Division (southern delta area) that 22% of samples exceeded 50  $\mu$ g L<sup>-1</sup>. UNDP/UNHS detected arsenic at concentrations greater than 50  $\mu$ g L<sup>-1</sup> in 4% of samples (125 samples) from Nyaungshwe of Shan State in southern Myanmar (UNDP/UNCHS, 2001). The Water Resources Utilisation Department carried out a survey of groundwater in Sittway Township in the western coastal area, as well as Hinthada and Kyaungkone Townships close to the south coast of Myanmar (WRUD, 2001). In Sittway Township, salinity problems occur in some groundwaters and surface waters and most tubewells are less than 15 m deep as a result. Merck field test kits were used for the analysis of arsenic. In Hinthada and Kyaunkone Townships, well depths are typically around 30–50 m deep, although some deeper tubewells (55-70 m) were also sampled. In the southern townships of the delta area, high iron concentrations are noted. The distribution of arsenic concentrations determined by 2001 is given in Table 4. Exceedances above 50  $\mu$ g L<sup>-1</sup> in shallow tubewells from Sittway, Hinthada and Kyaunkone Townships were around 10-13%. One sample from the depth interval 56-70 m also exceeded 50  $\mu$ g L<sup>-1</sup>. As with a number of other affected aquifers, dug wells from the WRUD survey generally had arsenic concentrations of  $<10 \ \mu g \ L^{-1}$  (WRUD, 2001).

More recent results from WRUD surveys have shown 15% of groundwater samples exceeding 50  $\mu$ g L<sup>-1</sup> (8937 analyses by April 2002). In these, dug wells were found to exceed 50  $\mu$ g L<sup>-1</sup>

Township	Well type	Number of samples (%)			Total samples
	•JP•	$< 10 \ \mu g \ L^{-1}$	10–50 $\mu g L^{-1}$	$>50 \ \mu g \ L^{-1}$	5 ann proc
Sittway	STW	17 (29.3)	35 (60.3)	6 (10.3)	58
-	DW	22 (96)	1 (4)	0 (0)	23
Hinthada	STW	56 (68.3)	15 (18.3)	11 (13.3)	82
	DW	6 (75)	1 (12.5)	1 (12.5)	8
Kyaungkone	STW	48 (80)	5 (8)	7 (12)	60
, ,	DW	21 (95)	1 (5)	0 (0)	22
	'DTW'	1 (33.3)	1 (33.3)	1 (33.3)	3

 Table 4. Frequency distribution of arsenic concentrations in groundwaters from the alluvial aquifer of Myanmar (from WRUD, 2001).

STW: shallow tubewell, DW: dug well, 'DTW': deep tubewell (55–70 m)

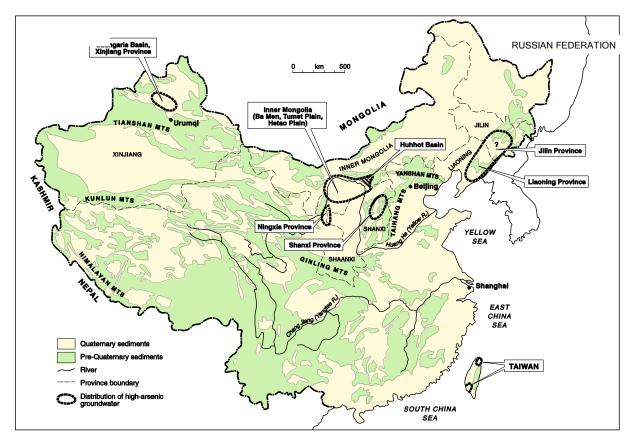
in 8% of samples. As the analyses from the various surveys were carried out using Merck field-test kits, the accuracy of the results is uncertain but likely to be limited. As with many other areas, the arsenic concentrations of the groundwaters of Myanmar have not been mapped in detail and investigations are in the reconnaissance stages. However, the Divisions/States of Ayerarwaddy, Bago (delta area) as well as Mon and Shan appear to be the worst-affected.

### Quaternary aquifers, Taiwan

Health problems experienced in Taiwan have been the subject of much research since their initial discovery in the early 1960s and have formed the basis of many epidemiological risk assessments over the last 30 years or so. Taiwan is the classic area for the identification of black-foot disease (e.g. Tseng and others, 1968; Chen and others, 1985) and other peripheral vascular disorders but many other arsenic-related diseases have also been described from the area.

Despite being under considerable international scrutiny from an epidemiological perspective, there appears to have been little effort to understand the distribution or causes of arsenic problems in the aquifers of Taiwan. As a result, very little information is available for the region. High-arsenic groundwaters have been recognised in two areas: the south-west coastal area (Kuo, 1968; Tseng and others, 1968) and the north-east coast (Hsu and others, 1997). Kuo (1968) observed arsenic concentrations in groundwater samples from south-west Taiwan ranging between 10  $\mu$ g L<sup>-1</sup> and 1800  $\mu$ g L<sup>-1</sup> (mean 500  $\mu$ g L<sup>-1</sup>, n=126) with half the samples analysed having concentrations of 400–700  $\mu$ g L<sup>-1</sup>. An investigation by the Taiwan Provincial Institute of Environmental Sanitation found that 119 townships in the affected area had arsenic concentrations in groundwater of >50  $\mu$ g L<sup>-1</sup>, with 58 townships having >350  $\mu$ g L<sup>-1</sup> (Lo and others, 1977). In north-eastern Taiwan, Hsu and others (1997) reported an average arsenic concentration of 135  $\mu$ g L<sup>-1</sup> for 377 groundwater samples.

In the south-west, the high arsenic concentrations are found in deep (100–280 m) artesian well waters. The sediments from which these are abstracted are poorly documented, but appear to include deposits of black shale (Tseng and others, 1968). The groundwaters are likely to be strongly reducing as the arsenic is found to be present largely as arsenic(III) (Chen and others, 1994) and some of the groundwaters contain methane (Tseng and others, 1968) as well as humic substances. Groundwaters abstracted in north-eastern Taiwan are also reported to be artesian but more typically shallow, with a depth range of 16–40 m (Hsu and others, 1997). As found in several other countries, groundwater from shallow dug wells have low arsenic concentrations (Guo and others, 1994). This is probably a reflection of relatively oxidising conditions in the shallow parts of the aquifer immediately around the open wells.



**Figure 7.** Map of China showing the distribution of recognised high-arsenic (>50  $\mu$ g L<sup>-1</sup>) groundwaters and the locations of Quaternary sediments.

The arsenic problems of Taiwan are largely historical as alternative treated surface water supplies have been provided for the affected communities.

## Alluvial plains, northern China

The presence of endemic arsenicosis has been recognised in China since the 1980s and today the scale of the problem is known to be large. Arsenic problems related to drinking water have been identified in Quaternary aquifers in the Province of Xinjiang and more recently in parts of Inner Mongolia and Shanxi Province (Figure 7). Concentrations of arsenic up to  $4,400 \ \mu g \ L^{-1}$  have been found in groundwater from these affected areas. These areas represent large internal drainage basins in arid and semi-arid settings.

Groundwater conditions in the arsenic-affected areas appear to be strongly reducing. Higharsenic drinking water has also been identified in parts of Liaoning, Jilin and Ningxia Provinces in north-east and north-central China (Sun, pers. comm., 2001) although the distribution and extent of these occurrences, the geological associations and the health consequences are not yet documented 50  $\mu$ g L<sup>-1</sup> (the Chinese standard) has been estimated as around 5.6 millions (Table 1) and the number of diagnosed arsenicosis patients currently around 20,000 (Sun and others, 2001). Mitigation measures are being implemented in some areas in China, including where possible the provision of piped low-arsenic surface water and in some cases the use of small-scale reverse osmosis plants. However, so far the mitigation efforts have covered relatively little of the area affected.

#### XINJIANG PROVINCE

The first cases of arsenic-related health problems due to drinking water were recognised in Xinjiang Province of north-west China (Figure 7). The region is arid with an average annual precipitation of less than 185 mm. The basin is composed of a 10 km thick sequence of sediments, including a substantial upper portion of Quaternary alluvial deposits. Artesian groundwater has been used for drinking in the region since the 1960s (Wang and Huang, 1994). Wang (1984) found arsenic concentrations up to 1200  $\mu$ g L<sup>-1</sup> in groundwaters from the province. Wang and Huang (1994) found concentrations of between 40  $\mu$ g L<sup>-1</sup> and 750  $\mu$ g L<sup>-1</sup> in deep artesian groundwater from the Dzungaria Basin on the north side of the Tianshan Mountains (up to 3800m altitude). The region stretches some 250 km from Aibi Lake in the west to Mamas River in the east. Artesian groundwater from deep boreholes (70–400 m) was found to have increasing arsenic concentrations with increasing borehole depth. Highest concentrations were also found in tubewells from the lower section of the alluvial plain. Many of these are believed to abstract groundwater from Ouaternary alluvial sediments but whether some of the deeper artesian wells abstract from older formations is not known. Shallow (nonartesian) groundwaters from wells in the depth range 2-30 m had observed arsenic concentrations between  $<10 \ \mu g \ L^{-1}$  and  $68 \ \mu g \ L^{-1}$  (average 18  $\mu g \ L^{-1}$ ). That in the saline Aibi Lake was reported as 175  $\mu$ g L<sup>-1</sup>, while local rivers had concentrations between 10  $\mu$ g L<sup>-1</sup> and  $30 \ \mu g \ L^{-1}$ .

Wang and others (1997) reported arsenic concentrations up to 880  $\mu$ g L<sup>-1</sup> from tubewells from the Kuitan area of Xinjiang. A 1982 survey of 619 wells showed 102 with concentrations of arsenic >50  $\mu$ g L<sup>-1</sup>. High fluoride concentrations were also noted in the groundwaters (up to 21.5 mg L<sup>-1</sup>).

## SHANXI PROVINCE

Investigations during the mid 1990s showed that arsenic in groundwater from wells in the Datong and Jinzhong Basins in Shanxi Province exceeded 50  $\mu$ g L<sup>-1</sup> in 837 (35%) out of 2373 randomly selected samples (Sun and others, 2001). Concentrations in Shanyin county, the worst-affected of the regions in Shanxi Province reached up to 4,400  $\mu$ g L<sup>-1</sup> (Sun and others, 2001).

#### YELLOW RIVER PLAIN, INNER MONGOLIA

In Inner Mongolia, concentrations of arsenic in excess of 50  $\mu$ g L<sup>-1</sup> have been identified in groundwaters from aquifers in the Hetao Plain, Ba Men region and Tumet Plain, the latter of which includes the Huhhot Basin (Figure 2.2, Luo and others, 1997; Ma and others, 1999). These areas are also arid with a mean annual precipitation of around 400 mm. The affected areas border the Yellow River Plain and include the towns of Boutou and Togto. In the region as a whole, around 300,000 residents are believed to be drinking water containing >50  $\mu$ g L<sup>-1</sup> (Ma and others, 1999). Arsenic-related health problems from the use of groundwater for drinking were first recognised in the region in 1990 (Luo and others, 1997). The most common manifestations of disease are skin lesions (melanosis, keratosis) but an increased

<b>Table 5.</b> Frequency distribution of arsenic concentrations in groundwater from the Huhhot Basin, Inner
Mongolia (Smedley and others, 2003).

Well depth	Number of samples (%)			Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50 \ \mu g \ L^{-1}$	sumpres
≤100 m	35 (59)	9 (15)	15 (25)	59
>100 m	6 (43)	0 (0)	8 (57)	14

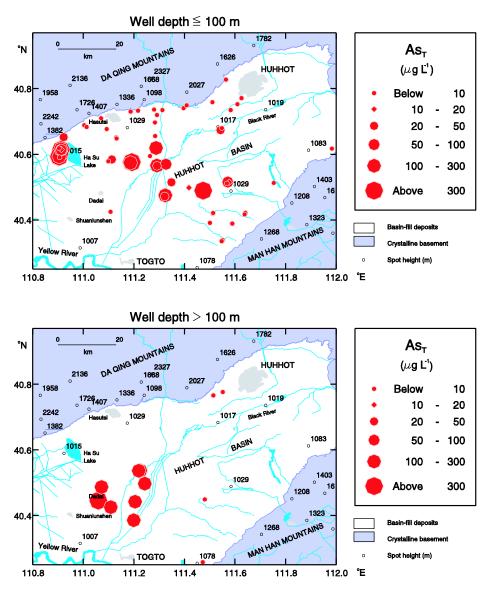


Figure 8. Regional distribution of arsenic in groundwaters from the shallow and deep aquifers of the Huhhot Basin (from Smedley and others, 2003).

prevalence of cancer has also been noted. Ma and others (1999) reported that 543 villages in Ba Men region and 81 villages in Tumet had tubewells with arsenic concentrations >50  $\mu$ g L<sup>-1</sup>. Around 1500 cases of arsenic disease had been identified in the area by the mid 1990s.

The Hetao Plain comprises a thick sequence of young unconsolidated sediments. In a study of groundwater from the Wuyuan and Alashan areas, Guo and others (2001) found that respectively, 96% and 69% of samples analysed had arsenic concentrations greater than 50  $\mu$ g L<sup>-1</sup>. Concentrations were generally much higher in groundwater from tubewells (depth range 15–30 m) than from open dug wells (3–5 m depth) and the highest concentration recorded was 1350  $\mu$ g L<sup>-1</sup>.

The area of Ba Men with high-arsenic groundwater appears to be around 300 x 20 km in extent and the sediments are Quaternary lacustrine deposits. Wells were mostly installed in the late 1970s and well depths are typically 10–35 m. Arsenic concentrations have been found in the range 50–1800  $\mu$ g L<sup>-1</sup> (Ma and others, 1999) and around 30% of wells sampled had As concentrations >50  $\mu$ g L<sup>-1</sup>. The groundwaters are reducing with arsenic being dominantly

Sample	Water level	Well depth	DOC	Arsenic
	m	m	$mg L^{-1}$	$\mu g L^{-1}$
HB2	1.5	3.5	9.3	560
HB18	2.0	6	_	49
HB58	4.0	8	2.5	<1
HB4	2.0	9	11.4	200

 Table 6. Summary arsenic data for groundwater from dug wells in the high-arsenic groundwater region of the Huhhot Basin.

present as arsenic(III). Some contain high fluoride concentrations (average 1.8 mg  $L^{-1}$ ; Ma and others, 1999).

The Huhhot Basin (area around  $80 \times 60$  km) lies to the east of Ba Men area (Figure 8). The basin is surrounded on three sides by high mountains of the Da Qing and Man Han ranges and is itself infilled with a thick sequence (up to 1500 m) of poorly consolidated sediments, largely of Quaternary age (Smedley and others, 2003).

Groundwater has been used for several decades for domestic supply and agriculture. Traditional sources of water were shallow dug wells that were typically 10 m or less deep and tapped the shallowest groundwater. These have now generally been abandoned in favour of tubewells which abstract at shallow levels (typically <30 m) by hand-pumps or in some cases by motorised pumps. Groundwater is also present within a distinct, deeper aquifer (typically >100 m depth). Tubewells tapping this deeper aquifer are often artesian in the central parts of the basin.

Arsenic concentrations in the Huhhot Basin groundwaters range between <1 and 1480  $\mu$ g L<sup>-1</sup> in the shallow aquifer ( $\leq 100$  m) and between <1 and 308  $\mu$ g L<sup>-1</sup> in the deep aquifer (>100 m). Of a total of 73 samples, summarised by Smedley and others (2003), 25% of shallow sources and 57% of deep sources have arsenic concentrations in excess of 50  $\mu$ g L<sup>-1</sup> (Table 5). The regional distributions of arsenic in the groundwaters from the shallow and deep aquifers are shown in Figure 8. Concentrations in the aerobic groundwaters from the basin margins are universally low. High concentrations are generally restricted to the low-lying part of the basin where groundwaters are strongly reducing (Smedley and others, 2001; Smedley and others, 2003). The redox characteristics of the Huhhot Basin groundwaters have many similarities with those of Bangladesh and it is logical to conclude that the main geochemical processes controlling arsenic mobilisation are similar in the two areas.

Of a limited number of samples of dug-well water investigated, some are observed to have arsenic concentrations in excess of  $50 \ \mu g \ L^{-1}$  (Smedley and others, 2003). The affected wells are from the part of the aquifer with high concentrations in tubewell waters. This observation contrasts with the situation observed in other reducing groundwater environments such as Taiwan (Guo and others, 1994) and the Bengal Basin (Smedley and others, 2003). The dug-well waters of the Huhhot Basin appear to be reducing with high concentrations of dissolved organic carbon (DOC, up to 11.4 mg L<sup>-1</sup>). This, together with the fact that low-lying parts of the basin are zones of groundwater discharge, rates of groundwater recharge are low and stabilisation of arsenic in solution (Smedley and others, 2003).

## Red River Plain, Vietnam

Arsenic problems have emerged only recently in the aquifers of the Red River Plain of northern Vietnam. Recent suggestions are that arsenic-related health problems are beginning to be identified among the exposed populations of Vietnam, although this is as yet

	Number of samples (%)			Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50~\mu g~{ m L}^{-1}$	$>50~\mu{ m g~L}^{-1}$	
Tong (2001) Holocene	117 (45)	62 (24)	81 (31)	260
Tong (2001) Pleistocene	84 (40)	70 (33)	56 (27)	210
Tong (2002) undivided	740 (60.2)	335 (27.3)	153 (12.5)	1228

**Table 7.** Summary arsenic data for groundwater from tubewells in the Red River Plain, Vietnam, divided into those from the Holocene and Pleistocene aquifers (from Tong, 2001; Tong, 2002).

unsubstantiated. The total area of the plain is around 17,000 km<sup>2</sup>. Groundwater is abstracted from unconsolidated Quaternary alluvial sediments which comprise up to 150 m of sand, silts, clay and some conglomerates. A superficial aquifer of Holocene sediments is around 10–40 m thick in the centre of the plain but thins to just 1–3 m on the margins (Tong, 2002). Underlying Pleistocene sediments form the main aquifer of the region and are around 100 m thick in the centre and south-east of the plain (Berg and others, 2001; Tong, 2002).

Private tubewells have generally been installed over the last decade and these abstract water via hand-pumps from shallow levels in the aquifer (<45m depth). Public-supply tubewells in the city of Hanoi abstract from the deeper Pleistocene aquifer (wells around 30–70 m deep). The lower aquifer is heavily pumped and has resulted in a seasonal drawdown of around 30 m around the centre of Hanoi (Trafford and others, 1996). Water-level drawdown of up to 1 m per year has been observed in some wells in Hanoi (Tong, 2002). Drawdown of the shallow aquifer has also occurred but a significant head difference exists between the two aquifers, suggesting that the two are not hydraulically connected (Tong, 2002). This appears not to be the case north-east of Hanoi, between the Red River and its tributary the Duong River, where poorly-permeable intervening layers between the Holocene and Pleistocene aquifers are thin or absent (Nguyen and Nguyen, 2002). Whether hydraulic separation between the aquifers occurs more widely in the plain is not known.

Groundwater is fresh in the upper parts of the plain but becomes more saline as a result of seawater intrusion in the lower reaches. Recent overpumping of the aquifers in the urban areas has also been linked to increasing saline intrusion (Tong, 2002). Many of the groundwaters of the region have high iron and manganese concentrations and some also contain high ammonium concentrations (Trafford and others, 1996).

Arsenic concentrations in the range  $1-3050 \ \mu g \ L^{-1}$  (average 159  $\mu g \ L^{-1}$ ) were reported by Berg and others (2001) for groundwater from the Hanoi area and surrounding rural areas. In a surveyed area of some 1000 km<sup>2</sup> around Hanoi, they found that the arsenic concentrations were spatially variable, but generally higher to the south of the city on the southern margins of the Red River. Concentrations were found to be high in groundwaters from both the shallow and deeper aquifers, but the extremely high values were found in the shallow groundwater from private tubewells. Groundwater from deeper tubewells had arsenic concentrations up to 440  $\mu g \ L^{-1}$ . Subsequent studies by Tong (2002) confirmed the high concentrations south of the city but also found some high concentrations to the west and east of the city. Concentrations were generally lower north of the Red River. Tong reported that from a survey carried out by the Geological Survey of Vietnam together with UNICEF in 1999, 153 samples out of 1228 (12.5%) in seven provinces had arsenic concentrations greater than 50  $\mu g \ L^{-1}$  (Table 7). An earlier report (Tong, 2001) indicated that arsenic concentrations are often high in groundwaters from both the Holocene and the underlying Pleistocene aquifers (Table 7).

The causes of the spatial variations are not fully clear, but differences in sediment thickness, composition and age and hydraulic connection between layers may be factors. In particular,

<b>Table 8.</b> Summary arsenic data for groundwater from tubewells in the Mekong Valley of Cambodia
(data from UNICEF and JICA: D. Fredericks, pers. comm., 2003).

	Number of samples (%)			Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50~\mu{ m g~L}^{-1}$	
Holocene aquifer	301 (50)	185 (31)	113 (19)	599
Pleistocene aquifer	1184 (95)	59 (5)	3 (0.2)	1246
Crystalline rocks	708 (96)	24 (3)	2 (0.3)	734

sediments to the north of Hanoi with typically low groundwater arsenic concentrations, are predominantly of Pleistocene age and are relatively thin (Berg and others, 2001). One uncertainty in the distribution of the arsenic concentrations in the groundwaters of the region is the impact that anthropogenic activity may have had on the mobilisation of arsenic. Since some high concentrations have been found close to the city of Hanoi, it is possible that urban wastewater recharge to the aquifer may have had some impact on the arsenic distributions. This remains speculation and requires further investigation.

Berg and others (2001) and Tong (2002) have suggested that significant seasonal variations exist in arsenic concentrations in given wells in relation to strong water-level fluctuations. Berg and others (2001) found some very large temporal variations, with often higher concentrations in wells sampled in September (rainy season) than when sampled in December (dry season) or May (early rainy season). By contrast, Tong (2002) reported that more samples tended to exceed the national standard of 50  $\mu$ g L<sup>-1</sup> in the dry season than the rainy season. As the data were in the case of Berg and others (2001) not reported in relation to other parameters (e.g. rainfall, water level) and in the case of Tong (2002) are presented just as ranges and percentage exceedances, the variations are difficult to interpret and to verify. Subsequent monitoring by EAWAG and others (with more stringent sampling and analytical procedures) has revealed much less temporal variation, the greatest being found in wells close to the river bank (M. Berg, pers. comm., 2004). Results have not yet been documented.

Maps have been produced showing the distribution of arsenic in groundwater in the Hanoi area (Berg and others, 2001; Tong, 2002) but so far, mapping of the groundwater quality in the plain as a whole has not been carried out.

## Mekong Valley; Cambodia, Laos, Thailand and Vietnam

The Mekong River system is another large delta with potential for development of groundwater arsenic problems. So far few investigations have been carried out in the valley as a whole. Most investigation to date appears to have been carried out in Cambodia. The Mekong has a substantial proportion of its length within Cambodia and tubewells provide a significant source of potable supply in the country. Water testing for arsenic is ongoing and little information has so far been properly documented. A reconnaissance screening of around 100 tubewells from 13 provinces carried out by Partners For Development in 1999 included analysis of arsenic, fluoride, some trace metals and some pesticides. Approximately 9% of the samples analysed had arsenic concentrations >10  $\mu$ g L<sup>-1</sup>, with observed concentrations in the range 10–500  $\mu$ g L<sup>-1</sup>. Exceedances above 10  $\mu$ g L<sup>-1</sup> were found in 5 out of the 13 provinces investigated. The highest concentrations observed were from Kandal Province, close to Phnom Penh. Several districts in this province have a high percentage of wells with water containing arsenic in excess of the WHO guideline value (Feldman and Rosenboom, 2000). Since this initial screening, field testing using portable kits has identified groundwater sources with concentrations above 10  $\mu$ g L<sup>-1</sup> in two additional provinces. High iron and manganese concentrations and anaerobic conditions are a common feature of the groundwaters throughout the lowland areas of Cambodia.

**Table 9.** Summary arsenic data for groundwater from tubewells in the Mekong Valley of Laos (unpublished data, 2004, UNICEF).

	Number of samples (%)			Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50 \ \mu g \ L^{-1}$	_
Holocene aquifer	531 (78)	143 (21)	6(1)	680

More recently, UNICEF has been carrying out groundwater arsenic screening in the Mekong aquifers. A map of perceived 'arsenic risk' in groundwater has been produced based on geology (Figure 9). Areas of greatest perceived risk are those with Holocene sediments forming the main aquifer. Groundwater arsenic data produced by UNICEF and JICA for the region so far (June 2003) are summarised in Table 8. Around 19% of samples from the Holocene aquifer are found to contain arsenic at concentrations >50  $\mu$ g L<sup>-1</sup>. UNICEF and other organisations continue to support and carry out field testing using portable kits with supplementary laboratory analysis in Cambodia. A plan to blanket test wells in 1500 villages that abstract groundwater from Holocene sediments is currently being drawn up for the southern part of the country.

One noteworthy feature of the Cambodian Mekong results is that some of the highest arsenic concentrations have been found in urban areas, i.e. around Phnomh Penh. Whether this reflects an impact of urbanisation (increased groundwater pumping or increased inputs of pollutants such as organic carbon to the aquifers) is not known and is in need of further investigation.

As the Mekong Valley also covers parts of Laos, Thailand and Vietnam, arsenic problems are also possible in the alluvial and deltaic parts of these countries. However, few data are so far available from these regions to assess the scale of the problem there. Doan (undated) provided some arsenic data measured by spectrophotometry for groundwater samples from the

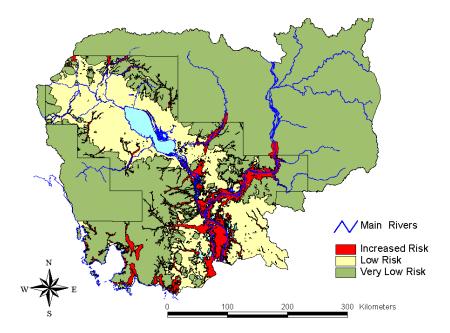


Figure 9. Geological map of Cambodia showing the distribution of potentially high-arsenic aquifers. Areas of perceived 'increased risk' are those with aquifers of Holocene age; areas of perceived 'low risk' are Pleistocene aquifers; areas of 'very low risk' are crystalline basement rocks (map source: UNICEF, Cambodia; D. Fredericks, pers. comm. 2003; geological units are provisional and accuracy of national boundaries is not guaranteed).

District	Number of samples (%)			Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50 \ \mu g \ L^{-1}$	*
Gujrat	33 (87)	3 (8)	2 (5)	38
Jhelum	32 (86)	4 (11)	1(3)	37
Chakwal	63 (88)	9 (12)	0 (0)	72
Sargodha	49 (83)	7 (12)	3 (5)	59
Attock	68 (92)	68)	0 (0)	74
Rawalpindi	81 (96)	3 (4)	0 (0)	84
Total	326 (90)	30 (8)	6 (2)	364

 Table 10. Frequency distribution of arsenic concentrations in groundwater samples from northern

 Punjab (from Iqbal, 2001).

Holocene, Pleistocene and Pliocene aquifers of the Mekong delta area of Vietnam. Concentrations were found to be mostly low, with only one sample exceeding 50  $\mu$ g L<sup>-1</sup>. Concentrations were in the range  $<1-5 \mu$ g L<sup>-1</sup> for groundwaters from Holocene deposits (9 samples, depth range 4–19 m),  $<1-32 \mu$ g L<sup>-1</sup> for those from Middle and Upper Pleistocene deposits (39 samples, depth range 5–120 m),  $<1-7 \mu$ g L<sup>-1</sup> for groundwater from Lower Pleistocene deposits (12 samples, depth range 113–191 m) and  $<1-57 \mu$ g L<sup>-1</sup> for groundwater from Pliocene deposits (39 samples, depth range 85–330 m). Highest concentrations in this Pliocene aquifer were in the Ben Tre area of the central Mekong delta. The Pleistocene and Pliocene sediments are the most exploited aquifers in the region. The Holocene sediments appear to be largely low-yielding aquitards and are not heavily used. Doan (undated) reported that UNICEF carried out some qualitative arsenic testing of Mekong groundwaters in Vietnam but did not detect arsenic.

UNICEF have also carried out some preliminary testing of groundwater from wells in Attapeu, Savannakhet, Champassak, Saravan, Sekong, Khammuane and Bolikamxay areas of Laos. Results from 200 samples reported by Fengthong and others (2002) suggested that some samples had arsenic concentrations greater than  $10 \ \mu g \ L^{-1}$  but that only one exceeded 50  $\ \mu g \ L^{-1}$ . The highest concentration observed in the region was  $112 \ \mu g \ L^{-1}$  (Attapeau province). To date, UNICEF in collaboration with the government and ADRA have tested some 680 samples from drinking-water sources and found 1% of sources having arsenic concentrations >50  $\ \mu g \ L^{-1}$  (Table 9, unpublished data).

#### Indus Plain, Pakistan

Quaternary sediments, mainly of alluvial and deltaic origin, occur over large parts of the Indus Plain of Pakistan (predominantly in Punjab and Sindh Provinces) and reach several hundred metres thickness in some parts (WAPDA/EUAD, 1989). Aquifers in these sediments are potentially susceptible to high groundwater arsenic concentrations. The Indus sediments have some similarities with the arsenic-affected aquifers of Bangladesh and West Bengal, being Quaternary alluvial-deltaic sediments derived from Himalayan source rocks. However, the region differs in having a more arid climate, greater prevalence of older Quaternary (Pleistocene) deposits and dominance of unconfined and aerobic aquifer conditions, with greater apparent connectivity between the river systems and the aquifers. Aerobic conditions are demonstrated by the presence of nitrate (Mahmood and others, 1998; Tasneem, 1999) and dissolved oxygen (Cook, 1987) in many Indus groundwaters. Hence, the aquifers appear to have different redox characteristics from those of the lower parts of the Bengal Basin. Under the more aerobic conditions (and near-neutral pH), arsenic mobilisation in groundwater should be less favourable.

Aquifer	Number of samples (%)			Total samples
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50 \ \mu g \ L^{-1}$	
Surface water	1 (4)	2 (8)	20 (83)	24
Groundwater from shallow aquifer (<15 m)	7 (30)	7 (30)	9 (39)	23
Groundwater from deeper aquifer (>15 m)	9 (69)	2 (15)	2 (15)	13

 Table 11. Frequency distribution of arsenic concentrations in water from Ron Phibun area (from Williams and others, 1996).

To date, only a limited amount of groundwater testing for arsenic has been carried out in Pakistan. However, the Provincial Government of Punjab together with UNICEF began a testing programme in northern Punjab in 2000. Districts to be tested were selected on the basis of geology and available water-quality information. These included areas affected by coal mining and geothermal springs (Jhelum and Chakwal Districts), areas draining crystalline rock (Attock and Rawalpindi), areas with high-iron groundwaters (Sargodha) and one district from the main Indus alluvial aquifer (Gujrat). A total of 364 samples were analysed. The majority (90%) of samples had arsenic concentrations less than 10  $\mu$ g L<sup>-1</sup>, although 6 samples (2%) had concentrations above 50  $\mu$ g L<sup>-1</sup> (Table 10) (Iqbal, 2001). Further well testing for arsenic is on-going. No confirmed cases of arsenic-related disease have been found in Pakistan, although epidemiological investigations are also being undertaken in some areas. From the available data, the scale of arsenic contamination of Indus groundwaters appears to be relatively small although further results are needed to verify the region affected. Quaternary aeolian sand deposits occur to the east of the Indus Plain (Thar and Cholistan desert areas) as well as over large parts of the Baluchistan Basin of western Pakistan. Testing of abstraction tubewells in these areas is also required. Under the arid conditions in Pakistan, high fluoride concentrations and high salinity appear to be more widespread water-related problems than arsenic.

## MINING AND MINERALISED AREAS

#### Ron Phibun, Thailand

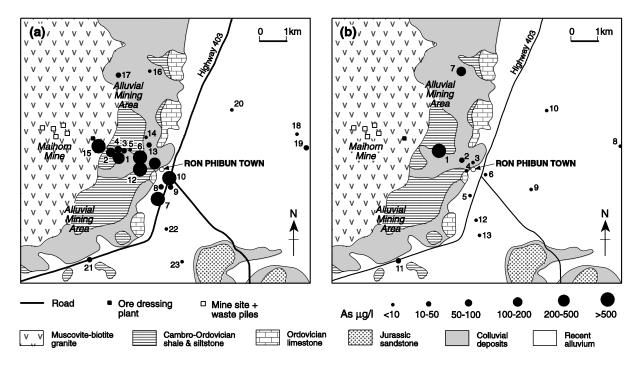
Health problems related to arsenic have been well-documented in Thailand, in this case related to mineralization and mining activity rather than alluvial and deltaic aquifers. In terms of documented health problems from drinking water, Ron Phibun District in Nakhon Si Thammarat Province in peninsular Thailand represents the worst known case of arsenic poisoning related to mining activity (Figure 10). Health problems were first recognised in the area in 1987 and over 1000 people have been diagnosed with arsenic-related skin disorders. particularly in and close to Ron Phibun town (Williams, 1997). At the time of first recognition of the problems, some 15,000 people are thought to have been drinking water with  $>50 \ \mu g \ L^{-1}$ arsenic (Fordyce and others, 1995). The affected area lies within the South-East Asian Tin Belt. Primary tin-tungsten-arsenic mineralisation and alluvial placer tin deposits have been mined in the district for over 100 years, although mining activities have now ceased. Legacies of the mine operations include arsenopyrite-rich waste piles, waste from ore dressing plants and disseminated waste from small-scale panning by villagers. Remediation measures include transportation of waste to local landfill. Waste piles from former bedrock mining are found to contain up to 30% arsenic (Williams and others, 1996). Alluvial soils also contain high concentrations of arsenic, up to 0.5% (Fordyce and others, 1995).

High arsenic concentrations found in both surface and shallow groundwaters from the area around the mining activity are thought to be caused by oxidation of arsenopyrite, made worse by the former mining activities and subsequent mobilisation during post-mining rise in groundwater levels (Williams, 1997).

Surface waters draining the bedrock and alluvial mining areas are commonly acidic (pH<6) with SO<sub>4</sub> as the dominant anion (up to 142 mg L<sup>-1</sup>) and with high concentrations of some trace metals, including aluminium (up to 10,500  $\mu$ g L<sup>-1</sup>), cadmium (up to 250  $\mu$ g L<sup>-1</sup>) and zinc (up to 4200  $\mu$ g L<sup>-1</sup>; Williams and others, 1996). Strong positive correlations are observed between SO<sub>4</sub> and Cd, Al, Be, Zn and Cu. Also, SO<sub>4</sub> correlates negatively with pH (Fordyce and others, 1995). These associations suggest strongly that arsenic and the associated trace metals are derived by oxidation of sulphide minerals. Concentrations of the trace metals diminish downstream of the mining area. Highest arsenic concentrations (up to 580  $\mu$ g L<sup>-1</sup>) were found some 2–7 km downstream of the bedrock mining area (Williams and others, 1996).

Shallow groundwaters (<15 m) are from alluvial and colluvial deposits and deeper (>15 m) groundwaters are from an older carbonate aquifer. The shallow aquifer shows the greatest contamination with arsenic, with concentrations up to 5100  $\mu$ g L<sup>-1</sup> (Figure 10). In the shallow aquifer, 39% of samples collected randomly had arsenic concentrations >50  $\mu$ g L<sup>-1</sup>, while in the deeper aquifer, 15% exceeded 50  $\mu$ g L<sup>-1</sup> (Table 11; Williams and others 1996).

The high-arsenic groundwaters of the Ron Phibun area clearly differ from many other higharsenic groundwater provinces in Asia. In the shallow aquifer, conditions are more oxidising than those prevalent in the worst-affected areas of Bangladesh and West Bengal for instance. The differences reflect the distinct geochemical reactions that are controlling the groundwater arsenic concentrations (Section 0). In the groundwaters from the deeper aquifer of Ron Phibun, conditions appear more similar to those from other high-arsenic aquifers in Asia and



**Figure 10.** Simplified geology of the Ron Phibun Area, Thailand showing the distribution of arsenic in analysed groundwaters (from Williams and others, 1996). The distributions are (a) arsenic in groundwater from shallow tubewells (<15 m depth), (b) arsenic in groundwater from deeper tubewells (>15 m). Numbers refer to samples given in Williams and others (1996).

<b>Table 12.</b> Frequency distribution of arsenic concentrations in groundwater from Chowki block,
Madhya Pradesh, India (from Chakraborti and others, 1999).

Block	Nu	Number of samples (%)		
	$< 10 \ \mu g \ L^{-1}$	$10-50 \ \mu g \ L^{-1}$	$>50~\mu g \ L^{-1}$	
Chowki	109 (75)	25 (17)	12 (8)	146

the maintenance of arsenic in solution appears to be more of a function of the presence of reducing conditions, although leakage of high-arsenic water from the overlying shallow aquifer is also a possibility.

## Rajnandgaon District, Madhya Pradesh, India

Water-related arsenic problems first became recognised in Rajnandgaon District, Madhya Pradesh in 1999. Concentrations in groundwater samples from the worst-affected village, Kondikasa, in Chowki block, have been found to range between  $<10 \ \mu g \ L^{-1}$  and  $880 \ \mu g \ L^{-1}$  (Chakraborti and others, 1999). Out of 146 samples analysed, 8% were found to contain more than 50  $\mu g \ L^{-1}$  arsenic (Table 12). Three of these exceeding samples were from dug wells, one containing a concentration of 520  $\mu g \ L^{-1}$ . Most were from tubewells which were usually less than 50 m deep (range 10–75 m). Arsenic-related skin disorders have been recognised in a number of the villagers. Gold mining activity has taken place in the local area, though the extent of mining and of mineralisation is not documented. To date, no maps have been produced of Chowki block to indicate the distribution and scale of the problem.

## Other areas

Although many areas of mining and mineralisation exist in South and East Asia, few have been documented and the distribution of groundwater arsenic concentrations related to them is unknown. High concentrations were noted in some surface waters and groundwaters close to the Bau mining area of Sarawak, Malaysia (Breward and Williams, 1994), although there is no evidence that affected waters are used for drinking water. Arsenic is a well-known risk in sulphide mineralised areas and hence the locations of such problems can be reasonably well predicted. Despite many mining-related problems, modern mining practices are designed to minimise environmental impacts. Environmental protection measures include criteria for siting and management of waste piles, control of effluents and treatment of acid mine drainage.

# Hydrogeochemistry of arsenic

#### **OVERVIEW**

There has been a considerable increase in the amount of research carried out on arsenic in groundwater and the environment over the last few years and understanding of the processes involved has improved as a result of studies carried out in Asia and elsewhere. However, many aspects of the mechanisms of release are still poorly understood. Our ability to predict the variations with time is limited, yet temporal variations in arsenic concentration are a central issue to mitigation. Below are outlined what we know of the principal causes of arsenic mobilisation in water and the environment and the information that is available concerning spatial and temporal variability in the arsenic-affected aquifers of Asia.

It has been seen (Section 0) that the highest concentrations of arsenic tend to occur in sulphide minerals and metal oxides, especially iron oxides. It therefore follows that where these occur in abundance, arsenic problems can result if the release from the minerals is favoured. Under most circumstances, the mobilisation of arsenic in surface waters and groundwaters is low because of retention in these mineral sinks. However, the toxicity of arsenic is such that it only takes a very small proportion of the solid-phase arsenic to be released to produce a groundwater arsenic problem. There are a number of drivers that can result in the release of arsenic from minerals and the build-up of detrimental concentrations in water. These are outlined in broad terms below.

#### ARSENIC SOURCES

Arsenic occurs naturally in all minerals and rocks, although its distribution within them varies widely. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. Most are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment. The greatest concentrations of them occur in mineral veins. The most abundant arsenic ore mineral is arsenopyrite (FeAsS). This is often present in ore deposits, but is much less abundant than arsenian pyrite (Fe(S,As)<sub>2</sub>) which is probably the most important source of arsenic in ore zones. Other arsenic sulphides found in mineralised areas are realgar (AsS) and orpiment (As<sub>2</sub>S<sub>3</sub>).

Though not a major component, arsenic is also present in varying concentrations in common rock-forming minerals. As the chemistry of arsenic follows closely that of sulphur, the other, more abundant, sulphide minerals also tend to have high concentrations of arsenic. The most abundant of these is pyrite (FeS<sub>2</sub>). Concentrations of arsenic in pyrite, chalcopyrite, galena and marcasite can be very variable but in some cases can exceed 10 weight % (Table 13). Besides being an important component of ore bodies, pyrite is also formed in low-temperature sedimentary environments under reducing conditions. It is present in the sediments of many rivers, lakes and oceans as well as a number of aquifers. Pyrite is not stable in aerobic systems and oxidises to iron oxides with the release of sulphate, acidity, arsenic and other trace elements. The presence of pyrite as a minor constituent in sulphide-rich coals is ultimately responsible for the production of 'acid rain' and acid mine drainage, and for the presence of arsenic problems around coal mines and areas of intensive coal burning.

High concentrations of arsenic are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or adsorbed to surfaces. Concentrations in iron oxides can also reach weight percent values (Table 13), particularly where they form as the oxidation products of primary iron sulphides. Adsorption of arsenate to hydrous iron oxides is

Mineral	As concentration range (mg kg <sup>-1</sup> )		
Sulphide minerals:			
Pyrite	100-77,000		
Pyrrhotite	5–100		
Marcasite	20–126,000		
Galena	5–10,000		
Sphalerite	5-17,000		
Chalcopyrite	10-5000		
Oxide minerals:			
Haematite	up to 160		
Fe oxide (undifferentiated)	Up to 2000		
Fe(III) oxyhydroxide	up to 76,000		
Magnetite	2.7–41		
Ilmenite	<1		
Silicate minerals:			
Quartz	0.4–1.3		
Feldspar	<0.1–2.1		
Biotite	1.4		
Amphibole	1.1–2.3		
Olivine	0.08-0.17		
Pyroxene	0.05–0.8		
<b>Carbonate minerals:</b>			
Calcite	1–8		
Dolomite	<3		
Siderite	<3		
Sulphate minerals:			
Gypsum/anhydrite	<1-6		
Barite	<1-12		
Jarosite	34–1000		
Other minerals:			
Apatite	<1–1000		
Halite	<3–30		
Fluorite	<2		

**Table 13.** Typical arsenic concentrations in rock-forming minerals (from Smedley and Kinniburgh, 2002 and references therein).

known to be particularly strong. Adsorption to hydrous aluminium and manganese oxides may also be important if these oxides are present in quantity (e.g. Peterson and Carpenter, 1983; Brannon and Patrick, 1987). Arsenic may also be adsorbed to the edges of clays and on the surface of calcite. However, the loadings involved are much smaller on a weight basis than for the iron oxides. Adsorption reactions are responsible for the low concentrations of arsenic found in most natural waters.

Arsenic is also present in many other rock-forming minerals, albeit at comparatively low concentrations. Most common silicate minerals contain around 1 mg kg<sup>-1</sup> or less. Carbonate minerals usually contain less than 10 mg kg<sup>-1</sup> arsenic (Table 13).

Rocks, sediments and soils contain variable concentrations of arsenic but, not surprisingly, the highest concentrations tend to be found in materials with abundant sulphide and oxide minerals. Fine-grained sediments such as shales, mudstones and their unconsolidated equivalents tend to contain the highest concentrations of arsenic. A summary of typical concentration ranges in common rocks, sediments and soils is given in Table 14. Typical

Classification	Rock/sediment type	Arsenic range
Classification	Rock/scument type	$(mg kg^{-1})$
Igneous rocks	Ultrabasic rocks	0.03–16
-	Basic rocks	1.5-110
	Intermediate	0.09–13
	Acidic rocks	0.2–15
Metamorphic rocks	Quartzite	2.2-7.6
-	Hornfels	0.7-11
	Phyllite/slate	0.5-140
	Schist/gneiss	<0.1–19
	Amphibolite/greenstone	0.4–45
Sedimentary rocks	Shale/mudstone	3–490
	Sandstone	0.6-120
	Limestone	0.1-20
	Phosphorite	0.4–190
	Iron formations and iron-rich sediment	1–2900
	Evaporite deposits	0.1-10
	Coal	0.3-35,000
	Bituminous shale	100-900
Unconsolidated	Sediments	0.5-50
sediments and soils		
	Soils	0.1–55
	Soils near sulphide deposits	2-8000

**Table 14.** Typical arsenic concentration ranges in rocks, sediments and soils (from Smedley and Kinniburgh, 2002 and references therein).

arsenic concentration ranges in rocks, sediments and soils (from Smedley and Kinniburgh, 2002 and references therein).

Arsenic is also introduced to the environment through a number of human activities. Apart from mining activity and the combustion of fossil fuels which involve redistribution of naturally occurring arsenic, concentrations in the environment can increase through the manufacture and use of arsenical compounds such as pesticides, herbicides, crop desiccants and additives in livestock feed, particularly for poultry. The use of arsenical pesticides and herbicides has decreased significantly in the last few decades, but their use for wood preservation and feed additives is still common. The use of CCA as a wood preservative may be banned in Europe in the coming years. The environmental impact of using arsenical compounds can be major and long-lasting, although the effects of most are relatively localised. Most environmental arsenic problems recognised today are the result of mobilisation under natural conditions.

#### PROCESSES INVOLVED IN MOBILISATION

#### **Oxidation of sulphide minerals**

Many mining areas with an abundance of sulphide minerals demonstrate the environmental effects of sulphide-mineral oxidation. Acid-mine drainage is one notable consequence. Oxidation of pyrite by atmospheric oxygen can be described by the reaction:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+.$$

The overall oxidation reaction leads to the generation of iron oxide  $(Fe(OH)_3)$  and dissolved sulphate  $(SO_4)$  as well and the production of acid  $(H^+)$ . The oxidation can also lead to the

release of trace metals and arsenic into solution. Even larger quantities of arsenic can be released from arsenic sulphide minerals such as arsenopyrite (FeAsS). However, the strong adsorption capacity of iron oxides (especially the freshly formed, poorly crystalline oxides) together with the tendency for acidic conditions, normally mean that dissolved arsenic concentrations diminish at some distance downstream. Although a significant source of arsenic exists locally to produce an aqueous arsenic problem in such areas, the local geochemical conditions are usually unsuitable to maintain it.

The effects of sulphide mineral oxidation have also been seen in mineralised aquifers as a result of lowering the water table and introducing atmospheric oxygen to the aquifer. Probably the best example to demonstrate this is the mineralised sedimentary aquifers of Wisconsin, USA. Here, historical abstraction of groundwater has led to aquifer dewatering and the accumulation of concentrations of arsenic up to 12,000  $\mu$ g L<sup>-1</sup> in the groundwater at the levels of the mineralised veins (Schreiber and others, 2000). Oxidation of sulphide minerals has been advocated strongly by many workers in West Bengal (e.g. Das and others, 1994) as the cause of groundwater arsenic problems in the Bengal Basin. It is well-known that authigenic sulphide minerals can form under strongly reducing conditions in sediments in aquifers, lakes and marine settings. Generation of groundwater arsenic problems if these are allowed to oxidise is a reasonable hypothesis. However, the evidence for this mode of occurrence in the aquifers of the Bengal Basin is lacking. It is possible that such oxidation processes could be involved in some parts of the aquifers, particularly at the shallowest levels, for instance the depths penetrated by dug wells. However, it is not considered to be the main cause of the groundwater arsenic problems in the Bengal Basin or other sedimentary aquifers in Asia where the major arsenic problems exist. Indeed, groundwater in most dug wells from the Bengal Basin has low arsenic concentrations.

#### **Release from iron oxides**

#### RELEASE UNDER REDUCING CONDITIONS

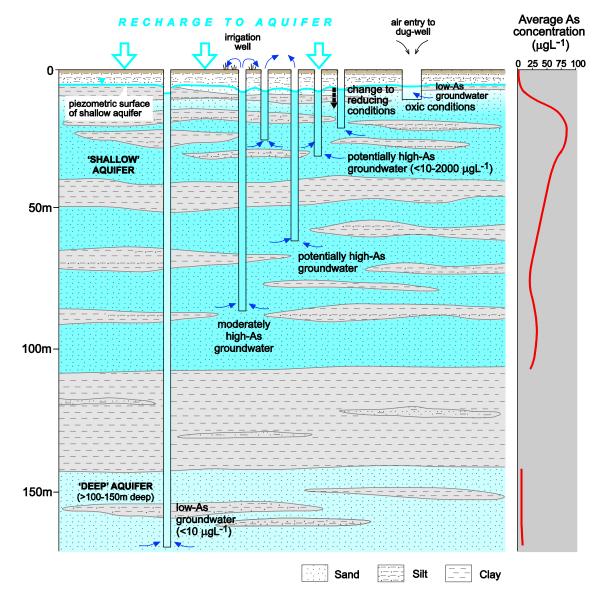
One of the main conclusions from recent research studies has been that desorption or dissolution of arsenic from iron oxides is an important or even dominant control on the regional distributions of arsenic in water. The onset of reducing conditions in aquifers can lead to a series of changes in the water and sediment chemistry as well as in the structure of the iron oxides. Many of these changes are poorly understood on a molecular scale. Some critical reactions in the change to reducing conditions and to subsequent arsenic release are likely to be the reduction of arsenic from its oxidised (As(V)) form to its reduced (As(III)) form. Under many conditions, As(III) is less strongly adsorbed to iron oxides than As(V) and reduction should therefore involve a net release from adsorption sites. Dissolution of the iron oxides themselves under reducing conditions is another potentially important process. Additional influences such as competition from other anionic solutes (e.g. phosphate) for adsorption sites, may also be important. It is notable for example, that reducing aquifers such as those of Bangladesh (BGS and DPHE, 2001), West Bengal (McArthur and others, 2004) and China (Smedley and others, 2003) have relatively high concentrations of dissolved phosphate. These are sometimes in excess of  $1 \text{ mg L}^{-1}$  and almost always in excess of the concentrations of dissolved arsenic.

The onset of reducing conditions in aquifers may result from rapid burial, particularly evident in areas of rapidly accumulating sediment (e.g. deltas). Burial of organic matter along with the sediments facilitates microbial activity which plays an important role in the generation of the reducing conditions (e.g. BGS and DPHE, 2001; McArthur and others, 2001). The role of microbes in the reduction and mobilisation process has been increasingly recognised in recent

years (Oremland and others, 2002; Islam and others, 2004). Several species of microbes have been found to be capable of dissimilatory arsenate reduction and a number of others are capable of arsenate reduction as a detoxification mechanism (Hoeft and others, 2002).

The nature of the organic matter involved in the generation of reducing conditions in arsenicaffected aquifers has been disputed in recent years. Some have cited disseminated finegrained solid and dissolved organic matter as the key redox driver (e.g. BGS and DPHE, 2001), others cite occurrences of peat (McArthur and others, 2001) while some have suggested that recent anthropogenic organic carbon is responsible (Harvey and others, 2002). Whatever the origin, the importance of organic matter in controlling the redox conditions in reducing aquifers such as those of the Bengal Basin is widely acknowledged.

The rates of the arsenic release reactions under reducing conditions are likely to be dependent on a number of factors including rates of sedimentation and diffusion of gases as well as microbial reactions, but they are likely to be relatively rapid on a geological time scale. The onset of reducing conditions and release from iron oxides is believed to be the main process



**Figure 11.** Schematic diagram of the aquifers in southern Bangladesh showing the distribution of arsenic and the configuration of wells.

controlling the high arsenic concentrations in the sedimentary aquifers of Asia.

In the groundwaters from the shallow aquifer of Bangladesh, the highest and most variable concentrations of arsenic occur in strongly reducing groundwaters below the redox boundary (zone over which the groundwater changes from oxidising to reducing conditions, usually just a few metres below the piezometric surface (Figure 11). Dug wells typically penetrate the shallowest levels of aquifers where conditions are relatively oxidised. Tubewells usually penetrate to deeper levels than dug wells in order to obtain better groundwater yields (although depths are usually the minimum required to achieve this). Entry of air to the open large-diameter wells also helps to maintain their relatively oxidised status in most circumstances (except in stagnant groundwater conditions with excess organic matter). Under most conditions therefore, groundwater in dug wells is likely to have relatively low arsenic concentrations as a combined function of shallow depth and the nature of the well construction.

#### RELEASE AT HIGH PH

Under aerobic and acidic to neutral conditions characteristic of many natural environments, adsorption of arsenic (as As(V)) to iron oxides is normally strong and aqueous concentrations are therefore usually low. However, the sorption is less strong at high pH. Increases in pH (especially above pH 8.5 or so) will therefore result in desorption of arsenic from oxide surfaces and a resultant increase in dissolved concentrations. Such processes are considered to have been responsible for the release of arsenic in oxidising Quaternary sedimentary aquifers in the arid inland basins of Argentina (Smedley and others, 2002) and south-western USA (Robertson, 1989) for example. Similar conditions have not been found to date in Asian sedimentary aquifers but the process may take place in some areas (e.g. arid regions of China or Pakistan).

#### Release from other metal oxides

Although more research has been done on arsenic and its association with iron oxides, aluminium and manganese oxides can also adsorb arsenic and may be additional sources or

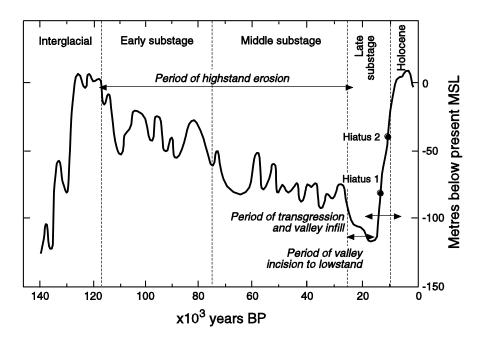


Figure 12. Sea-level changes during the last 140,000 years (after Pirazzoli, 1996).

#### Box 4. Frequently asked questions

# Why are arsenic concentrations often high in the shallow aquifers of Bangladesh but usually low in the deep aquifer?

This question is difficult to answer for certain because little information currently exists on the geology and hydrogeology of the deep aquifer. Limited data available so far suggest that the older (deeper) sediments are lithologically different. They are often brown in contrast to the overlying sediments, which are variable but commonly grey. The colour changes suggest changes in redox conditions, the deeper sediments being relatively oxic. Differences in hydrogeological history are also likely to be significant. Older sediments at depth have undergone longer periods of groundwater flushing. During the last glacial maximum around 12,000 years ago, relative sea level would have been much lower than its present level, resulting in steeper groundwater gradients and more active groundwater flow. Young (Holocene) sediments overlying these deposits have been deposited in post-glacial times, have not had such a long history of flushing and have not been subject to such large relative sea-level fluctuations. They also contain freshly-formed minerals which may be highly prone to reaction under reducing aquifer conditions.

#### Why are concentrations in groundwater from deep aquifers in other areas not always low?

In contrast to Bangladesh, deep aquifer sediments of unknown but likely Pleistocene age in Inner Mongolia (China) contain groundwater with sometimes high arsenic concentrations. In these, the sediment lithology is poorly defined as few geological studies have been carried out. It is likely that these have not been well-flushed since deposition since the area is an internal drainage basin which would not have been so greatly influenced by past sea-level fluctuations. The deep aquifers of Inner Mongolia are thought to be occupied by very slow-moving groundwater.

#### Are the arsenic concentrations in wells going to improve or deteriorate with time?

At present, there are insufficient data to define the nature of variability in individual wells over periods of days to weeks to years and more monitoring data are needed to define the temporal trends. Mixing of waters with different compositions will necessarily involve changes in arsenic concentration but on what scale and over what period are uncertain. Such changes will involve decreases as well as increases. Variations are likely to be greater at shallow depths than at deeper levels because groundwater flow is more active near the water table and inputs greater. In the first instance, it is reasonable to assume that an initial arsenic concentration (provided it is analytically reliable) will be representative for a given well and that it will not change significantly in the short-term.

sinks for arsenic if present in quantity in any given aquifer. They are likely to be less significant than iron oxides in controlling arsenic concentrations in groundwater, but cannot be ignored, and have been cited as potential sources of arsenic in some aquifers, including those from Bangladesh and Argentina.

#### **Groundwater flow and transport**

Geochemical conditions suitable for arsenic release are important in generating groundwater arsenic problems but the problems will only remain if the arsenic is not flushed away by moving groundwater over time. Another feature of many of the high-arsenic groundwater provinces of Asia is slow groundwater movement. A combination of young sediments (often <10,000 years old) and slow rates of aquifer flushing (e.g. low rates of recharge, poor sediment permeability, low hydraulic gradients) mean that arsenic accumulated through geochemical processes has not been flushed from the aquifer during its evolutionary history. This argument has been used in part to explain why the deep (Pleistocene) aquifers of

Bangladesh and other near-coastal aquifers have low arsenic concentrations. During pre-Holocene times, it is known that glacial conditions were associated with long-term low relative sea-level (up to 120 m below those of the present day; Figure 12). This would have resulted in greater head gradients in the past and more active groundwater movement (Box 4). It has been suggested that the deep aquifer has had a longer history of flushing during the pre-Holocene past and that solute arsenic accumulated in the past has been flushed from the aquifer over time (DPHE/BGS/MML, 1999; BGS and DPHE, 2001). Interestingly, such steep head gradients would not have affected inland basins such as those of northern China and so deep aquifers in such areas would not have been subject to such active groundwater flow during past ice ages.

It is also likely that sediments of the older deeper aquifers are mineralogically and texturally distinct from the younger Holocene deposits, a factor which may have a bearing on the groundwater arsenic concentrations. Certainly in Bangladesh, evidence suggests that the deeper Pleistocene sediments are dominantly more brown in colour than the Holocene deposits and therefore appear to be more oxidised. More work on the sediment chemistry of the deep aquifers of the Bengal Basin is required to investigate this further.

#### Impact of man's activities

A relevant question that has not been fully answered by the various studies of arsenic occurrence in South and East Asia is the extent to which man's activities have contributed to the arsenic problems in different situations. It is clear that in sulphide mining areas, man has had a major impact in exacerbating the problem by excavating ore minerals, redistributing waste piles and pumping mine effluent for instance. However, in sedimentary aquifers, the relationships are much less clear cut. Scientists working in West Bengal in the 1990s were of the opinion that the arsenic problem was of recent origin and related to the dewatering and oxidation of sedimentary aquifers containing pyrite (or arsenopyrite) through overabstraction of groundwater for irrigation of rice crops. Convincing evidence for this has never been produced, and subsequent studies in the Bengal Basin have related the occurrence of arsenic to the presence of naturally strongly reducing conditions coupled with slow groundwater movement. From this conclusion, it follows that the arsenic phenomenon is not recent but originated from the time of sediment burial and the onset of reduction. The arsenic in Bangladesh groundwaters may therefore have been present for hundreds to thousands of years (BGS and DPHE, 2001).

That is not to say that no impact can be expected from man's activities. The impacts of pumping on groundwater flow mean that some changes to the aquifer systems are likely in the medium to long term. Quantifying those impacts is difficult. There are various dimensions to the potential human influences, including the impacts of pumping-induced flow on transport of arsenic both within and between aquifers, impact of pollutants such as organic carbon and phosphate on aquifer redox and sorption/desorption reactions and impact of seasonal waterlogging of soils for rice production on sub-surface redox conditions.

It is interesting for instance that arsenic problems in the Red River delta of Vietnam are close to southern Hanoi and those of Cambodia close to Phnomh Penh. Whether this reflects a bias in regional testing or real highs in urban areas compared to rural areas is still open to question. Disposal of urban wastewater including sewage along open drains has been documented for Hanoi for example (Trafford and others, 1996). Harvey and others (2002) concluded that groundwater arsenic problems in part of Bangladesh were related to the introduction of organic carbon to the aquifer from surface pollutants. However, the evidence presented for this was unconvincing and the conclusion has sparked much subsequent debate. The impacts on groundwater quality of the human influences described above have received insufficient attention in past studies and require further investigation in order to ensure that groundwater resources will be sustainable and protected.

#### **'AT-RISK' AQUIFERS**

The previous sections indicate that many uncertainties exist over the spatial distribution of arsenic problems in groundwaters of Asia and elsewhere. However, sufficient information is available on the recognised high-arsenic groundwater provinces to allow them to be broadly categorised in terms of geology, hydrogeology and the processes likely to be controlling

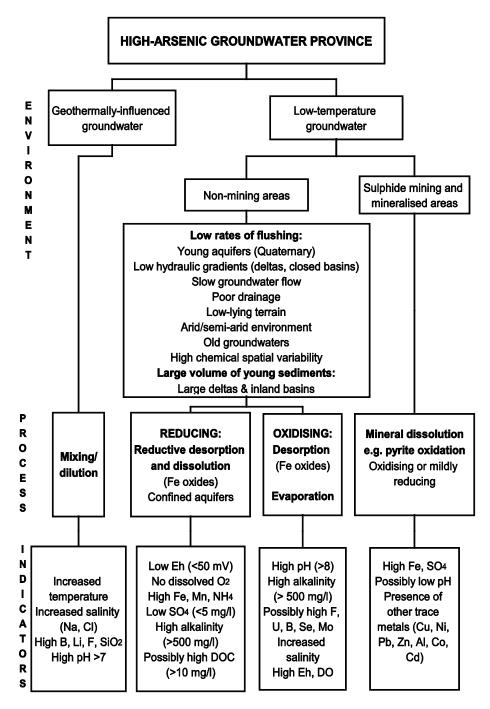


Figure 13. Classification of groundwater environments susceptible to arsenic problems from natural sources. Not all indicators of low flushing rates necessarily apply to all environments (from Smedley and Kinniburgh, 2002).

arsenic mobilisation.

A number of risk factors for the development of high-arsenic groundwaters were identified and summarised by Smedley and Kinniburgh (2002). These are highlighted in Figure 13. While no single factor is likely to be sufficient to identify likely at-risk aquifers, combinations of factors can be of value in pinpointing areas deserving increased priority for groundwater chemical analysis.

In arsenic-affected aquifers of Asia, some notable parallels in geology and hydrogeology are identifiable. Apart from areas related to bedrock mineralisation and mining activity (Ron Phibun, Thailand; Madhya Pradesh, India), and localised areas of geothermal activity, the documented cases included above are from young (Quaternary) sedimentary aquifers of alluvial, deltaic or lacustrine origin. Sediments rich in iron oxides may be particularly susceptible. In such aquifers, the presence of reducing conditions appears to be a key factor in determining on a regional scale where high groundwater arsenic concentrations will occur. Groundwaters with, for example, high concentrations of iron, manganese and ammonium will therefore be more likely to have high concentrations of arsenic than those with low concentrations. Where data for these are available, they can act as warning signs of potential arsenic problems, although as noted above, they cannot be taken as direct indicators of arsenic concentrations of sulphate and high concentrations of dissolved organic carbon can also be of use in defining reducing aquifers (Figure 13).

Slow groundwater movement is also a common feature of the identified high-arsenic groundwater provinces of Asia and elsewhere. Aquifers with limited recharge, or low hydraulic gradients are likely to have slow groundwater flow.

Aquifer size and sedimentation rate may also be relevant criteria in determining groundwater quality. The Bengal Basin is one of the largest and most rapidly accreting sediment basins in the world and the rapid burial of organic matter along with sediments (restriction of air access) may accelerate the onset of reducing conditions.

Arsenic problems have also been found in oxidising conditions in some arid and semi-arid inland (closed) basins. As noted above, these groundwaters are typically characterised by high pH (>8) and are accompanied by high salinity. High concentrations of trace elements such as fluoride, molybdenum and boron are also characteristic. While none of the oxidising, high-pH groundwater provinces recognised so far is from Asia, this is not to say that such conditions will not occur. Major deposits of Quaternary sediments (including loess) cover large parts of northern China for example. Quaternary aeolian deposits of Pakistan, including the Baluchistan Basin also contain high-pH groundwater. It is believed that the groundwaters in these have not been tested for arsenic.

One of the key findings of the last few years has been that the affected sedimentary aquifers of Asia (e.g. Bangladesh, China) do not have anomalously high concentrations of arsenic in the sediments. This is important because it implies that potentially any young sediments could develop groundwater arsenic problems, given a combination of geochemical conditions conducive to the release of arsenic (reducing conditions or oxidising, high-pH conditions) and hydrogeological conditions that prevent it from being flushed from the aquifer. Other alluvial and deltaic plains such as the lower reaches of the Yellow River Plain and Yangtze River of China and the Chao Phraya River of Thailand deserve further investigation.

#### VARIABILITY IN ARSENIC CONCENTRATIONS

#### **Spatial variability**

A high degree of spatial variability in arsenic concentrations both areally and with depth has been noted in many of the recognised problem aquifers. Such variability is a natural consequence of sediment heterogeneity and poor mixing brought about by sluggish groundwater movement. Notable vertical variations in sediment texture, composition and grain-size have been observed from sediments in Bangladesh on a scale of centimetres. This can have large impacts on groundwater movement between layers, on water-rock interactions and on local redox conditions. Small differences in depth of closely spaced wells can result in the tapping of different horizons (Figure 11). Lack of homogenisation of groundwaters and poor hydraulic connection between layers can maintain chemical differences on local scales. Besides, it should be borne in mind that in terms of thresholds of acceptability, the difference between concentrations of  $10 \ \mu g \ L^{-1}$  and  $50 \ \mu g \ L^{-1}$  is critical, yet geochemically the differences are very small.

Many high-arsenic groundwaters appear to be associated with occurrence of finer-grained and iron-oxide rich deposits, such as accumulate preferentially in low-lying distal parts of deltas or in low-flow zones of river floodplains. The occurrence of local arsenic hotspots observed in Bangladesh aquifers for instance, may be explained by the localised occurrence of fine-grained sediments in inside meanders and ox-bow lakes. Together with locally slow groundwater movement in these areas, this may be responsible for the build-up (and lack of flushing) of arsenic.

#### Temporal variability

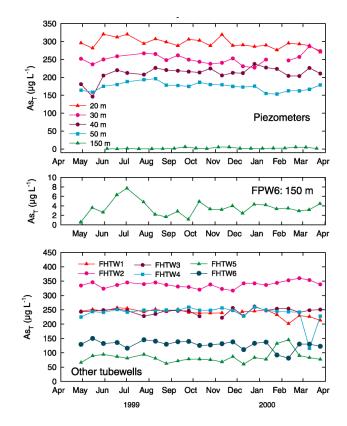
#### HIGH-ARSENIC AQUIFERS

The timescales over which temporal variations in arsenic concentrations may exist range from hours (diurnal changes) through seasons to years or decades. The potential causes of such changes are also variable: changes in groundwater pumping rate over the course of a day; seasonal variations in recharge, irrigation abstraction and head gradients; long-term changes in pumping regimes and climate. During the seasonal or annual cycle of a major abstraction source such as an irrigation well or municipal-supply well, the chemical composition of abstracted groundwater may be affected by the variable contribution from different depths which changes with time. Initial discharge tends to be dominated by flow from the shallowest horizons with deeper flow becoming more important with time as the cone of groundwater depression deepens. This influence is likely to be less important for small hand-pumped tubewells which individually involve much smaller abstractions. Changes in chemical compositions over longer timescales may result from long-term changes in groundwater level. To date, there has been very little investigation of the temporal variations in groundwater chemistry in high-arsenic aquifers from Asia and much more needs to be done to assess whether variations are significant in a practical sense. In Bangladesh, BGS and DPHE (2001) did not find evidence of significant temporal variation during fortnightly monitoring of groundwater from specially drilled piezometers over the course of a year. An example of this monitoring is given for Faridpur in central Bangladesh in Figure 14. Little variation was found either at shallow (tens of metres) or deep (150 m) levels. Continued monitoring of these piezometers after the completion of the BGS and DPHE project could have revealed useful information on the temporal variations over longer timescales, but unfortunately this was not carried out. As with the BGS and DPHE (2001) results, Tareq and others (2003) did not find significant seasonal variation in groundwater arsenic concentrations in 10 shallow tubewells from Bangladesh. Variations in arsenic concentration monitored pre-monsoon, syn-monsoon and post-monsoon were in the range 10–16% and largely within analytical error.

Few time-series data are documented for the groundwaters of West Bengal and as with Bangladesh, there remains uncertainty over whether significant temporal variations in arsenic concentration occur. They may occur in some places and not others. CGWB (1999) concluded from West Bengal groundwaters that groundwater arsenic concentrations vary seasonally, with minima during the post-monsoon period, considered to be due to dilution of groundwater by monsoon recharge. However, the conclusion is apparently based on small sample sets (4–6 samples at any given location) collected over a short time interval (less than one year). Chatterjee and others (1995) noted a variation of around 30% in time-series data from monitoring of groundwaters over the period of a year in their study of parts of 24 Parganas North and South, but detected no significant seasonal changes in the variation.

#### DEEP (OLDER) AQUIFERS

It has often been said in relation to the deep aquifers of the Bengal Basin that some wells that



**Figure 14.** Monitoring data for groundwater from selected wells and specially drilled piezometers in Faridpur area, central Bangladesh (from BGS and DPHE, 2001).

were once arsenic-free have become contaminated with time (e.g. Mandal and others, 1996). However, documentation and data in support of this conclusion are difficult to find. Since the long-term trends in groundwater arsenic concentrations are a critical issue for the sustainability of the deep aquifers, the data that indicate such variations need to be documented properly and be open to peer review. If temporal trends are apparent in groundwater from deep aquifers, there are a number of reasons why this may be the case. These include inadequate sealing of tubewells, multiple screening of tubewells at different depths to improve yields, as well as natural hydraulic connectivity between aquifers (as stated above). They also may represent analytical problems. A statistical approach is needed in interpreting time-series data.

#### DUG WELLS

Few time-series data exist for dug wells in arsenic-affected areas. Arsenic concentrations in dug wells may be susceptible to temporal change as the groundwaters abstracted from them are from the shallowest levels and therefore subject to the largest changes in recharge inputs, pollutant inputs and redox changes. They may also vary if particulate contents vary with time and water samples taken from them are not filtered. Despite these possibilities, groundwater in 3 dug wells from north-west Bangladesh monitored by BGS and DPHE (2001) over the course of a year showed little statistically significant variation. Concentrations were low and in the range  $0.5-2 \ \mu g \ L^{-1}$ , with only two individual measurements from the wells exceeding  $10 \ \mu g \ L^{-1}$ . More data are clearly needed to determine whether significant temporal changes occur in other areas, particularly where local groundwater arsenic concentrations are high. The relative contributions of particulate and dissolved fractions should also be investigated by measurement of other parameters (notably iron) as well as arsenic.

#### ARSENIC IN SURFACE WATER

Little information is available on the arsenic concentrations of surface waters in regions with high groundwater-arsenic concentrations. Even less is available on temporal variations. The greater likelihood of high suspended loads in surface waters means that the concentrations are potentially more variable than in most groundwaters as the arsenic associated with particles can be significant. Concentrations in particles are likely to be in the range  $5-10 \text{ mg kg}^{-1}$ , in line with the concentrations of 'average' sediments, but may be higher in iron-rich particles. There is also potential that river waters will vary seasonally as a result of the variations in the proportion of baseflow compared to runoff. This has not been studied in detail. However, most of the evidence points to surface waters generally having low arsenic concentrations, even where groundwater arsenic concentrations are high.

# Groundwater management for drinking water and irrigation

#### **OVERVIEW**

The previous sections highlight the extreme variability in arsenic concentrations both within and between aquifers and have shown some of the issues associated with identifying safe sources of water and determining suitable alternatives. One of the key developments of the past few years has been the realisation that the mode of occurrence of arsenic in water can vary substantially. The mechanisms of arsenic occurrence in water in mining and mineralised areas can be very different from those in young sedimentary aquifers and their distribution and scale can also differ considerably. Some of the options for water supply are detailed further in this section, along with the risks associated with them and potential strategies for dealing with those risks. The choice of water supply in any given area must depend on many technical and social factors that need to be assessed locally.

#### MINING AND MINERALISED AREAS

In areas with rich deposits of sulphide minerals, both surface waters and groundwaters are potentially vulnerable to high arsenic concentrations. Other toxic trace elements may also be present in excessive concentrations (e.g. copper, lead, zinc, cobalt, cadmium, nickel). In these areas, surface waters, groundwaters and soils are all potentially affected by high arsenic concentrations. However, the scale of contamination is likely to be localised, on the scale of a few kilometres around the site of mineralisation. Mitigation of the problem therefore centres on identifying contaminated water sources and finding alternative supplies locally. Both identification of at-risk sources and mitigation should be less of a problem than in arsenicaffected sedimentary aquifers. Environmental problems are usually exacerbated by mining activity and are therefore largely predictable.

#### **SEDIMENTARY AQUIFERS**

#### Shallow groundwater

#### SHALLOW TUBEWELLS

Of the sedimentary aquifers in South and East Asia with recognised arsenic problems, the majority are composed of young sediments at shallow depths, say less than 50–100 m or so. In Bangladesh, the highest concentrations and largest range of concentrations are found in the shallow aquifers which are dominantly of Holocene (<12,000 years) age. The extreme variability indicates that on a local scale, i.e. that relevant to mitigation, no reliable method can be used to predict their concentrations accurately and no substitute therefore exists for testing each well for arsenic if it is to be used for drinking water. This is not to say that on a regional scale some sort of prioritisation would not be possible given some knowledge of the distribution of sediment textures, hydrogeology and water chemistry. Bangladesh groundwaters tend to have highest arsenic concentrations in the low-lying parts of the delta. This is also evident in other aquifers of Asia (e.g. Huhhot Basin, China; Smedley and others, 2003). However, our understanding of the distribution of arsenic in groundwater at present does not allow prediction of such trends with confidence, even on a regional scale, and hence major testing programmes in such susceptible aquifers are needed regardless of local geological variations.

The distributions of arsenic in different districts of Bangladesh vary widely (BGS and DPHE, 2001). The worst-affected districts identified from the BGS and DPHE (2001) study were (percentage of samples with arsenic concentrations greater than 50  $\mu$ g L<sup>-1</sup> in parentheses): Chandpur (90%), Munshiganj (83%), Gopalganj (79%), Madaripur (69%), Noakhali (69%), Satkira (67%), Comilla (65%), Faridpur (65%), Shariatpur (65%), Meherpur (60%), Bagerhat (60%) and Lakshmipur (56%). In the worst-affected areas, it would probably be appropriate to abandon use of the shallow aquifer in the long-term in favour of alternative sources of drinking water.

On the other hand, on a national scale, the BGS and DPHE (2001) survey showed that for tubewells <150 m deep, 27% exceeded 50  $\mu$ g L<sup>-1</sup> and 46% exceeded 10  $\mu$ g L<sup>-1</sup>. This means that 73% and 54% of wells had concentrations below these limits respectively. Also, 24% of samples analysed had concentrations below the analytical detection limit, usually 0.25  $\mu$ g L<sup>-1</sup> or 0.5  $\mu$ g L<sup>-1</sup>. The districts of Thakurgaon, Barguna, Jaipurhat, Lalmonirhat, Natore, Nilphamari, Panchagarh and Patuakhali all had no samples with arsenic >50  $\mu$ g L<sup>-1</sup> in the survey. This means that large-scale abandonment of tubewells in many parts of Bangladesh is unnecessary. The same holds for most other sedimentary aquifers of Asia where arsenic problems have been encountered. Major investments have been made in shallow tubewells across Asia and in many places these still constitute a reliable source of safe drinking water. There is also the potential for segregation of wells for different uses. High-arsenic wells could be used for washing and other domestic purposes for example, provided the wells are labelled adequately.

In many areas with high-arsenic groundwater, domestic-scale treatment is being carried out in order to remove or reduce the arsenic in drinking-water supplies. These usually involve either aeration and sedimentation, coagulation and filtration, adsorption, ion exchange or membrane filtration (Edwards, 1994; Hering and others, 1996; Ahmed, 2003). While many of these techniques have been adapted for domestic use in affected areas and the technologies have improved significantly in recent years, issues remain over their sustainability and the disposal of high-arsenic waste products. They can provide a useful short-term solution in affected areas but are unlikely to form the basis of long-term mitigation strategies.

It should be borne in mind that the shallow high-arsenic groundwaters of the Bengal Basin and other areas of South and East Asia also often have problems with a number of other trace elements that can be detrimental to health (e.g. high manganese, uranium, boron concentrations) or can cause problems with acceptability (high salinity, iron, ammonium concentrations). In arid areas (e.g. northern China) the shallow aquifers can also have problems with high fluoride concentrations. These other elements rarely correlate well with arsenic and so shallow groundwaters with good quality in respect of arsenic concentrations may not necessarily be good quality in other respects. Defining acceptability criteria for potable water supplies should therefore involve consideration of other potentially detrimental constituents and not just arsenic.

#### DUG WELLS

It has been traditionally accepted that shallow groundwater from open dug wells usually has low concentrations of arsenic. Evidence from Bangladesh (BGS and DPHE, 2001), West Bengal (Chakraborti, 2001), Myanmar (WRUD, 2001) and Taiwan (Guo and others, 1994) indicates that many dug wells contain water complying with the WHO guideline value of  $10 \ \mu g \ L^{-1}$  and most comply with the national standards of 50  $\mu g \ L^{-1}$ .

Despite this tendency, a rather different situation is apparent for groundwater from dug wells in Inner Mongolia. As shown above, dug wells in the Huhhot Basin were found to contain groundwater with arsenic concentrations up to 560  $\mu$ g L<sup>-1</sup> in the area where tubewell arsenic concentrations were also high (Smedley and others, 2003). Some recent studies in Bangladesh and Myanmar also appear to be finding higher arsenic concentrations in dug wells than previously appreciated, although supporting evidence has not yet been published to verify this. Some of the higher concentrations observed may be due to particulate rather than dissolved arsenic and concentrations may therefore vary depending on the turbidity of the groundwaters. Particulate matter could presumably be removed by some simple filtration or settling.

The findings suggest that in any given aquifer, concentrations of arsenic in dug wells cannot be assumed to have acceptably low arsenic concentrations without a testing programme to confirm the concentration ranges. Care should also be taken in analysing for arsenic that the relative contributions of dissolved and particulate arsenic are determined.

Since traditional large-diameter dug wells are normally open to the atmosphere and tap the shallowest levels of the aquifer, they are also potentially vulnerable to contamination from bacteria and other surface pollutants. Well siting and construction are therefore important criteria for well protection. Locating wells at some distance from latrines and other contaminant sources is important, as is installation of adequate sanitary seals. Installation of hand-pumps removes potential contamination from introduced buckets and disinfection of water can give protection against waterborne diseases. Periodic cleaning of the well can help to reduce suspended material.

One of the major constraints on the use of dug wells is likely to be well yields. This is especially the case in areas with relatively large water-level fluctuations, where dug wells can dry up in the dry season. Poor water quality is linked to this to some extent, as particle settling becomes more difficult when wells dry up. Poor well yields may be the ultimate limit of the sustainability of dug wells in some areas. They are also not suitable in areas with thick layers of superficial clay.

Evidence from the BGS and DPHE (2001) study of Bangladesh suggests that dug wells also contain potentially detrimental concentrations of uranium (up to 47  $\mu$ g L<sup>-1</sup>). Dug wells had the highest concentrations of uranium identified in groundwaters from Bangladesh. Few epidemiological data exist to set a safe limit for uranium in drinking water, but new WHO guidelines include a provisional value for uranium of 9  $\mu$ g L<sup>-1</sup>. Concentrations of nitrate also exceeded the WHO guideline value in some wells, presumably as a result of surface pollution.

Hence for the reasons outlined above, dug wells may offer a suitable short-term solution to arsenic problems in some affected areas of Asia. However, they are unlikely to form a major component of long-term mitigation strategies for most areas.

#### Groundwater from deep/older aquifers

Although analyses of groundwater from deep aquifers in the Bengal Basin are still relatively limited, there appears sufficient information available to indicate that deep (older) aquifers in the region have much lower arsenic concentrations than many of the shallow aquifers above. The BGS and DPHE (2001) results suggested this for areas of south and east Bangladesh. CGWB (1999) found comparatively low concentrations in the deep aquifers of West Bengal. Van Geen and others (2003a) found similar results east of Dhaka. Data for other elements are also sparse, but where available, they suggest that concentrations of manganese, uranium and most other trace elements are also low in these deep aquifers. The older sediments therefore offer potentially good prospects as alternative sources of safe water for the Bengal Basin. Van Geen and others (2003a) reported successes with take-up of groundwater supplied by six newly installed 'deep' (60–140 m, but pre-Holocene) community wells in a badly affected

part of Bangladesh. In the short time since the wells have been installed, they are said to have proved popular with the local communities and women have been willing to walk up to hundreds of metres for their drinking water. The authors reported that such wells could provide drinking water for up to 500 people living within 150 m of the well in densely populated villages. Whether willingness to walk for supplies of drinking water would be a widespread phenomenon in arsenic-affected areas is untested and deserves further investigation.

Considerable uncertainties remain over the deep aquifers particularly with respect to i) their lateral extent; ii) their depth ranges (as demonstrated by the Van Geen and others (2003a) example); and iii) the variation in their hydraulic separation from the shallow aquifers. In many places these will not have been assessed if adequate supplies of water have been available at shallower depths.

An important risk with development of such deep (low-arsenic) aquifers is from potential drawdown of high-arsenic groundwater from shallower levels and contamination in the long-term (decades or longer). This can occur if intervening layers of clay are thin or absent, or if seals on wells penetrating the deep aquifer are inadequate. Flow modelling of the Bangladesh aquifers (BGS and DPHE, 2001) suggested that flow down to deep levels (100 m or more) is likely to be slow even under active pumping conditions. Modelling of aquifers in the Faridpur area of central Bangladesh suggested that rates of groundwater movement to a well screened at 110–135 m depth from the water table at a lateral distance of 500 m would be of the order of 200 years. The rate was found to be highly dependent on local lithology.

Detailed hydrogeological investigations are therefore an essential prerequisite to the development of such aquifers on a regional scale. The quality of well construction also needs to be high. Subsequent groundwater-quality monitoring for arsenic and a number of associated parameters also needs to be carried out. The greatest threat is from abstraction of large volumes of water for irrigation. Regulation of water abstraction should therefore be an integral part of water-management policy to protect the deep aquifers. Introduction of abstraction licensing would be a logical step in policy development. Recording of well log information in a systematic way for newly drilled deep tubewells would also improve the knowledge base on the aquifers.

It is clear from investigations in other regions of South and East Asia, that deep aquifers are not always low-arsenic aquifers. The Huhhot Basin of Inner Mongolia is a case in point. Here, groundwater from (probably) Pleistocene aquifers at 100–400 m depth contain arsenic concentrations in the range  $<1-308 \ \mu g \ L^{-1}$ . The variations reiterate the fact that aquifer depth is not an indicator of groundwater arsenic status. They also stress the need for detailed hydrogeological investigations in young sedimentary aquifers to identify sources and model their responses to groundwater development before any development takes place.

#### Surface water

#### RAINWATER

Of all the sources of drinking water available for communities, rainwater is the least likely to face problems with arsenic contamination. Concentrations of dissolved solids will usually also be very low (perhaps too low). Rainwater harvesting offers a potential source of drinking water for individual households in areas where other sources are unsuitable. The method requires a suitable roof for collection and storage tank with adequate sealing to protect it from bacterial and algal contamination. It has been estimated that about half of households in Bangladesh have roofs suitable for collection of rainwater (e.g. GI, tiled surfaces) but that

Water	Risk for supply	Mitigation strategy		
Туре		Household scale	Village scale	Urban scale
Shallow tubewells (Holocene aquifers)	High arsenic concentration	Water testing; alternative source if concentration high	Water testing; alternative source if concentration high	Alternative source/municipal treatment plant if concentration high
	High concs of other inorganic constituents (e.g. Mn, U, NH <sub>4</sub> , B)	Water testing; treatment difficult	Water testing; treatment difficult	Water testing; treatment plant
Deep tubewells (older sedimentary aquifers)	Drawdown of high-arsenic water from shallow aquifers	_	Carry out prior site investigations; restrict use to drinking water; regulate abstraction	Carry out prior site investigations; restrict use to drinking water; regulate abstraction
Dug wells	Poor yields if wells dry up seasonally	Occasional use; alternative source; walk to other wells	Relocate/deepen wells	-
	Bacterial and other waterborne diseases, high particulate loads	Disinfection, filtration	Well protection: sanitary seals, hand- pump installation, water disinfection, periodic cleaning. Relocate wells away from pollution sources	_
	Other inorganic water-quality problems (e.g. nitrate, uranium manganese)	Difficult	Water treatment difficult. Relocate wells away from pollution sources (nitrate)	-
	Arsenic may exceed prescribed limits	Water testing necessary. Treatment difficult	Water testing necessary. Treatment difficult	_
Surface water	Potential bacterial problems, high particulate loads	Small-scale water treatment (e.g. pond sand filters)	Small-scale water treatment (pond sand filters)	Urban water treatment plants
	Other pollutants (e.g. nitrate, pesticides)	Difficult	Difficult	Urban water treatment plants
Rainwater	Seasonal, difficult in arid areas	Partial supply	_	_
	Bacterial contamination	Storage protection, disinfection	-	_

**Table 15.** Risks associated with the use of drinking water from various sources at various scales and potential strategies to mitigate them.

many of the poorer families would not be suitably equipped (Ahmed and Ahmed, 2002). Rainwater harvesting can provide a seasonal supply of water for drinking but its period of use will be more limited in arid areas. Even so, provision of rainwater can still be beneficial even if available for only a few months of the year.

#### RIVERS, PONDS

Surface water usually has very low arsenic concentrations (typically  $<5 \ \mu g \ L^{-1}$ ). Exceptions include waters affected by mining activity and some geothermal areas. These are generally easily identified. As noted above, mining-contaminated waters are also usually localised to within a few kilometres of the mining activity (Smedley and Kinniburgh, 2002) although those affected by geothermal inputs can be more widespread.

Surface waters from the arsenic affected regions of South and East Asia usually have low concentrations. Indeed, this is why there are many proponents of treated surface water as an option for safe water supply in Bangladesh and elsewhere. BGS and DPHE (2001) found concentrations of  $<2 \ \mu g \ L^{-1}$  in five river samples from the affected areas of Bangladesh. A sixth sample, from the Mahananda River flowing through the Chapai Nawabganj arsenic hotspot area of western Bangladesh had a concentration of  $29 \ \mu g \ L^{-1}$  (March 1999) although repeat sampling (December 1999) gave a value of  $2.7 \ \mu g \ L^{-1}$ , an order of magnitude lower. Whether this difference represents real seasonal changes is difficult to assess on the basis of such limited data. It does highlight the possibility that dry-season groundwater discharge to the river systems could raise the surface water arsenic concentrations, especially in the worst-affected areas. Small rivers may be more affected than large rivers with greater volumes of water. However, oxidation of the reduced arsenic and consequent adsorption will lower the dissolved concentration being discharged to a large extent. The extent will depend upon the initial concentration and the river baseflow index (proportion of groundwater present) for instance.

A worse problem associated with the use of surface water is the potential risk from bacterial and other water-borne diseases arising from pollution. This problem means that surface water will probably always require adequate treatment to remove such hazards before use. At the village level, this has been achieved through the use of pond sand filters. At a municipal level, water treatment works can be installed for treatment of larger volumes. It is likely that any arsenic present in the initial waters will be removed by both of these treatment systems to concentrations below the drinking-water thresholds. Other potential problems with the quality of surface-water sources include inputs of nitrate and possibly organic compounds (pesticides, solvents) in some areas as a result of pollution. Concentrations of these will vary depending on local conditions and are difficult to remove by low-technology treatment methods.

## **Recommendations for surveying and monitoring**

#### **OVERVIEW**

Although our ability to predict arsenic concentrations in groundwater from a given area or aquifer is still rather limited, knowledge of its occurrence and distribution has improved greatly over the last few years. We therefore probably know enough about where high concentrations tend to occur to make reasonable estimates of likely at-risk aquifers on a regional scale. Young sediments in alluvial and deltaic plains and inland basins as well as areas of mining activity and mineralisation are obvious target areas for further evaluation. The guidelines for improving understanding of the arsenic problem and how to go about dealing with it are broadly the same in any region at increased risk from arsenic contamination. Firstly, the scale of the problem needs to be assessed. Secondly, where problems exist, it is necessary to find out whether or not the situation is becoming worse with time. Thirdly, where problems exist, it is necessary to identify the potential strategies or alternatives that are most appropriate for supplying safe (low-arsenic) water.

Central to these issues is arsenic testing. In any testing programme, it is important to distinguish between reconnaissance testing: that necessary for establishing the scale of a groundwater arsenic problem; and blanket testing: that required for compliance and health protection. Blanket testing involves the analysis of a sample of water from every well used for drinking water. For reconnaissance testing, the numbers of samples need not be large; they should however be collected on a randomised basis. Monitoring is the repeat sampling of a given water source in order to assess temporal changes over a given timescale (as distinct from repeat testing to cross-check analytical results).

The quality of analytical results is also paramount; analysis of arsenic in water is by no means a trivial task, yet reliable analytical data are key to understanding the nature and scale of groundwater arsenic problems as well as dealing with them. Instigation of any new arsenic testing or monitoring programme requires consideration of the analytical capability of the local laboratories. In some cases, development of laboratory capability (quality-assurance procedures, training, equipment upgrades, increased throughput, etc) may be required and should be built in to the testing programme.

Appropriate mitigation responses for arsenic-affected regions will necessarily vary according to local geological and hydrogeological conditions, climate, population affected and infrastructural factors. Surface water may or may not be available as an alternative. Other groundwater aquifers at different depths or in different locations may be available for use and need additional assessment. Decisions about what action to take in respect of the arsenic-affected aquifer depend on factors such as percentage of wells of unacceptable quality and range in concentrations (degree of exceedance above 50  $\mu$ g L<sup>-1</sup> or 10  $\mu$ g L<sup>-1</sup>). Below are outlined strategies for assessing the scale and distribution of arsenic problems in South and East Asian aquifers and for providing the necessary information as a basis for mitigation.

#### AQUIFER DEVELOPMENT AND WELL TESTING

#### Aquifers of 'low' potential risk

It follows from Section 0 above that our ability to define where low-arsenic aquifers are likely to be with accuracy is limited. Broadly, they are likely to include carbonate rocks, crystalline basement rocks and other old (pre-Quaternary) sediments that have not been affected by mineralisation or geothermal inputs. However, given the potential health risks associated with arsenic in drinking water, there is an argument for some randomised reconnaissance-scale testing of existing wells for arsenic in areas with little or no information, regardless of their perceived risk status (based on our current understanding). Provided the testing is random, survey results will provide information on the concentration ranges of arsenic to be expected in a given aquifer or region. Testing for arsenic alone may be sufficient in this case but other constituents of health concern could be included depending on available budgets (e.g. iron, manganese, fluoride, nitrate; electrical conductance would also be useful).

Newly drilled boreholes should also include analysis of arsenic, at least on a subset of samples. Identification of significant numbers of samples with unacceptably high arsenic concentrations (say >10  $\mu$ g L<sup>-1</sup>) should trigger a programme for more extensive chemical analysis and geochemical investigation. This should involve analysis of a wider suite of analytes aimed at identifying the causes as well as the scale of the arsenic problem. Until a more detailed understanding of the arsenic concentrations in groundwaters of different aquifers in the developing world (and elsewhere) is available, including arsenic as a chemical analyte is a logical cautious approach. Although correlations between arsenic and other elements (e.g. iron) have often been noted in groundwaters, the correlations are usually insufficiently good to rely on proxy analytes.

#### Potentially high-arsenic aquifers

As with any other area, aquifers at greater potential risk from high arsenic concentrations require the scale of any groundwater arsenic problem to be defined and the likelihood of future changes assessed. In undeveloped areas where little previous information is available and new groundwater-supply projects are planned, merely testing for arsenic will determine the scale of the problem but will not define the processes involved. These need to be established to understand the aquifer better and ensure that groundwater use will be sustainable and that subsequent investment is appropriate. There is therefore a need for a detailed hydrogeological and geochemical investigation before any project implementation. This may involve collation of all available hydrogeological data (e.g. well depths, water levels, aquifer physical characteristics, pumping rates, groundwater yields), collection of new water samples for more detailed chemical analysis (a more comprehensive range of analytes) and assessment of sediment chemistry and mineralogy. Such studies can be time-consuming and may have large cost implications. In some countries, local institutions may be equipped to carry out these investigations. In others, expertise from external organisations may be required. The size of the prior investigation work should be commensurate with the size of the intended water-supply programme, amounting to say 5-10% of the projected implementation cost.

In areas where groundwater is already in use but water-quality data are limited or absent, reconnaissance testing is necessary in the first instance to define the scale of any arsenic problem.

Defining the concentration ranges and spatial distributions of arsenic in groundwater is best achieved by some sort of randomised groundwater survey (most importantly, not based on previous knowledge of groundwater arsenic concentrations). The scale of groundwater testing should be commensurate with the numbers of people dependent on the water supply and potentially affected by it. In Bangladesh, the density of wells sampled in the BGS and DPHE (2001) national survey was 1 per 37 km<sup>2</sup>. The number of samples tested represented only around 0.05% of the tubewells believed to be present in Bangladesh. The survey proved inadequate to pick out many of the localised arsenic hotspots that occur in some areas but did serve to identify the worst-affected parts of the country and the depth ranges of the tubewells with the worst problems. It therefore highlighted priority areas for mitigation. These were

Area	Existing drinking-water wells	New drinking-water wells
Untested areas	Randomised reconnaissance groundwater arsenic survey. Scale of survey dependent on number of wells, areal extent of aquifer, number of people served. Stratified random approach (stratification based on geology, well depth). Blanket arsenic testing of wells used for public supply, schools, hospitals.	Initial hydrogeological and geochemical site/regional investigation. Test drilling; analysis of groundwater for arsenic during drilling and on completion.
Established groundwater arsenic problem areas	Blanket testing for arsenic.	Decision to drill new wells based on previous results. Alternatives necessary in badly-affected aquifers. In marginal cases, selection of well location, depth etc, based on previous information. Analysis for arsenic on completion.

Table 16. Arsenic testing strategies in potential high-arsenic groundwater provinces.

seen to be the south-eastern part of Bangladesh. Subsequent surveys by various organisations may have refined the data distributions, but to the best of my knowledge do not appear to have changed the overall conclusions concerning the worst-affected areas and hence the priority areas for mitigation.

The BGS and DPHE (2001) survey statistics indicated that 27% of shallow tubewells in Bangladesh had arsenic concentrations >50  $\mu$ g L<sup>-1</sup>. This figure compares well with an earlier estimate of exceedances above 50  $\mu$ g L<sup>-1</sup> for the whole country (26%) based on data from BGS, DPHE and other organisations (DPHE/BGS/MML, 1999). Of course, these data just provide summary statistics and define regional distributions and do not define concentrations in individual wells. This latter is needed for compliance testing. The BGS and DPHE (2001) survey showed the high degree of spatial variability in groundwater arsenic concentrations and, as with many other surveys, demonstrated the need for testing of individual wells used for drinking water.

Wells used for irrigation should also be tested ultimately as these represent a potential, though less direct and as yet unquantified, threat to health. They are however, of a lower priority.

Survey samples need to be georeferenced (latitude and longitude data or other national grid) and notes made of aquifer type, well depth , well age, well owner, well number if available and location. Other aquifers present in the region (e.g. the deep (Pleistocene) aquifer in Bangladesh) should also be tested on a randomised basis to assess their potential as alternatives. The data need to be analysed to assess whether statistically significant variations exist in variables such as well depth, well age and sediment type. The data should be incorporated into a database for ready storage and manipulation. The data should also be mapped.

In areas where some initial surveys have been carried out and where arsenic problems have been recognised, spatial patterns may be discernible. If these are significant, they should highlight where mitigation needs to be targeted and where not. Past experience shows that many arsenic-affected aquifers have highly variable groundwater arsenic concentrations on a local scale. In this case and where concentrations are high, blanket testing of wells will most probably be required. This is best achieved by laboratory analysis using reliable local facilities equipped for rapid throughput of samples. Where these are absent, facilities should be set up and equipped for analysis of arsenic and a range of other diagnostic elements (see below). Where setting up of laboratories is not possible or where the scale of testing is very large and facilities inadequate to cope with the scale of testing required (e.g. Bangladesh), field-test kits can be an alternative. The technology for these has improved in the last few years and while older kits were barely able to determine concentrations of arsenic at less than  $100 \ \mu g \ L^{-1}$ , the sensitivity of newer designs is better. Wherever possible, capability to test reliably at  $10 \ \mu g \ L^{-1}$  should be aimed for. Wherever possible, a subset of samples analysed by field-test kits (say 10%) should be cross-checked by a reliable laboratory analysis. A premium should be placed on reliability of analytical results and quality assurance should be a critical and ongoing undertaking with any groundwater testing or monitoring programme (Box 1).

Past hydrogeochemical investigations of high-arsenic aquifers have shown correlations with other elements but these are rarely sufficiently significant to be useful in a practical sense (e.g. iron, manganese). Results indicate that there are no suitable reliable proxy indicators for arsenic concentration in groundwater.

#### Deep aquifers below high-arsenic aquifers

As the deep (Pleistocene) aquifers of Bangladesh, West Bengal and Nepal are identified as being potentially suitable sources for drinking-water supply and also being vulnerable to contamination from above, it is important that future development of such sources on a major scale is preceded by detailed hydrogeological and hydrochemical investigations. These should include sedimentological studies to assess physical aquifer dimensions; pumping tests and groundwater flow modelling to determine flow mechanisms and assess the likelihood of drawdown from shallow levels; and testing of a wide range of chemical parameters to determine controlling processes and assess other elements of potential health concern.

During development of such deep aquifers, it is of importance to collate and document as much hydrogeological information as possible. In the case of Bangladesh for instance, collection of information such as sediment texture (sand, silt, clay) and sediment colour would be helpful and would demand little extra cost. Texture gives information on water storage capacity and sediment history. In the Bengal Basin, experience has shown that reddish-coloured sediments at depth are most likely to contain groundwater with low concentrations of arsenic and iron. Colour gives information on redox conditions and stratigraphy and can help date the aquifers. The redox conditions and aquifer age have both proven critical to the quality of water with respect to many other elements of health concern as well as arsenic. Databasing of such information is also important.

Collection of such information on these potentially valuable aquifers is of great importance, but should not serve to delay mitigation efforts in areas with recognised arsenic problems.

#### MONITORING

Monitoring can be a major and expensive task. Production of good analytical data is paramount and as stated above, analysis of arsenic is difficult (Box 1). Analytical problems should therefore be expected and variations viewed with scepticism until found to be statistically significant. As a first approximation, it is reasonable to assume that temporal changes will not be major in the short-term and that an initial analysis is likely to be representative for a given groundwater source (unless as stated above, the analysis is suspect). Hence, single analyses can give an indication of fitness for drinking water in the absence of time-series information. In general, larger fluctuations in chemical composition can be expected at shallower levels where groundwater throughputs are higher and compositions more strongly influenced by changing groundwater head gradients. Chemical compositions in deeper aquifers can be expected to be more stable and changes are likely to be dampened and over longer timescales, unless affected directly by flow (leakage) from other neighbouring aquifers.

#### Shallow sedimentary aquifers with recognised arsenic problems

On the scale of arsenic problems recognised in countries such as Bangladesh, even initial testing for arsenic is a major logistical and analytical undertaking. Compliance monitoring of tubewells and dug wells defined to be initially 'safe' is an even more demanding, and in many cases impossible, task. The scale of monitoring possible in any given region will depend on the numbers of operating drinking-water wells and the resources (funds, analytical capabilities) available. Monitoring should be of secondary priority to initial testing but is a necessary undertaking given the current uncertainty in temporal variations in arsenic concentrations. Monitoring is required not only for raw groundwater from shallow tubewells, but also dug wells (especially those with concentrations >50  $\mu$ g L<sup>-1</sup>, which should be retested to verify the concentration) and treated water having been through an arsenic-removal plant. Recent investigations have shown that not all treated groundwaters have acceptably low concentrations of arsenic (Mahmud and Nuruzzaman, 2003).

The concentration ranges chosen for monitoring wells vary according to the reason for monitoring. For compliance monitoring, priority would be appropriate for wells with concentrations of the order to  $10-50 \ \mu g \ L^{-1}$  and wells used for major public supply. For research purposes, monitoring of groundwater sources with concentrations outside this range (both low and high) would be of value.

The frequency of monitoring also depends on the objective of the monitoring exercise. Assessment of short-term (diurnal) changes requires frequent monitoring over a periods of hours. Observation of seasonal changes requires weekly of fortnightly monitoring. Longerterm changes require monitoring on the order of annually or biannually.

#### Deep (older) aquifers in arsenic-prone areas

The deep aquifers of the Bengal Basin represent a special case in that they appear to be largely free of arsenic and are a potentially important alternative source of drinking water, yet their vulnerability to contamination from the high-arsenic shallower aquifer is in large part untested. An important component of a groundwater protection policy for the deep aquifers of the Bengal Basin (and other aquifers vulnerable to such leakage from contaminated aquifers) is the regular monitoring of groundwater quality in order to detect any deterioration in the medium or long term and to take mitigating action if necessary. Annual or biannual monitoring of such tubewells used for public water supply would be appropriate. Arsenic would be the most important analyte but a range of other parameters (water level, electrical conductance, iron, manganese) would also be useful. Monitoring for these selected parameters should be conducted for several years (5 and preferably longer). That is not to say that the tubewells should not be used until a suitable run of time-series data have been collected. A subset of samples should also be tested for all health-related parameters. Such monitoring can be a large task, but the number of deep wells installed is likely to be much smaller than shallow hand-pumped tubewells.

#### Further research needed to assess temporal variations

Sufficient uncertainty remains over the temporal variations in arsenic concentrations in groundwaters in affected aquifers that research programmes need to be undertaken in specific areas to obtain further monitoring data. On a research scale, this is a relatively easy

programme to set up and could have been instigated in many of the affected areas shortly after their discovery. Accumulated data from the regular monitoring of selected wells over periods of months or a few years would have helped to identify the periodicity, scale and causes of any observed temporal variations and resolve many of the uncertainties which persist.

Ideally, a programme involving monthly monitoring of selected tubewells in affected areas (monitoring for arsenic as well as water level, electrical conductance, iron, manganese) should be undertaken in some areas in order to identify seasonal trends. Such monitoring should be over the course of several years (two minimum). Monitoring of groundwater quality at different depths in recognised high-arsenic aquifers is also required. Such programmes have been started in Bangladesh and elsewhere but more monitoring is needed to collect a larger body of time-series data. Studies of diurnal variations in heavily used tubewells are also required to establish water-quality variations over the course of days.

Little information is so far available on the temporal variation in arsenic concentration in dug wells. Specific monitoring programmes in a few shallow wells, sampled approximately monthly, can be carried out to establish temporal variations, especially in relation to water-level changes.

Seasonal monitoring of surface waters in areas with badly affected aquifers would help to establish whether temporal variations exist and whether they are sufficiently significant to cause consistent exceedances above national standards and the WHO guideline value. Monthly sampling of filtered (0.45  $\mu$ m pore size or less) river water over the period of a year would provide information on whether variations are significant in an operational sense. It is stressed that analysis of unfiltered water is likely to produce highly variable results depending on the turbidity of the water since arsenic analysis usually involved acidification, and at any given time the result will include suspended as well as dissolved arsenic.

many of the poorer families would not be suitably equipped (Ahmed and Ahmed, 2002). Rainwater harvesting can provide a seasonal supply of water for drinking but its period of use High arsenic concentrations recognised in many parts of Asia and elsewhere are dominantly found in groundwater and many of the health consequences encountered have emerged in relatively recent years as a result of the increased use of groundwater from tubewells for drinking and irrigation. In terms of numbers of groundwater sources affected and populations at risk, problems are greatest in Bangladesh, but major problems have also been identified in India (West Bengal, and more recently Bihar and Tripura), northern China, Vietnam, Taiwan, Thailand, Cambodia, Myanmar and Nepal. Occasional high-arsenic groundwaters have also been found in Pakistan, although the occurrences there appear to be less widespread. Higharsenic groundwaters in affected areas tend to be found in alluvial or deltaic aquifers or in inland basins. Hence, much of the distribution is linked to the occurrence of young (Quaternary) sediments in the region's large alluvial and deltaic plains (Bengal Basin, Irrawaddy delta, Mekong Valley, Red River delta, Indus Plain, Yellow River Plain). Although groundwater arsenic problems have been detected in some middle sections of the Indus and Mekong Valleys, such problems have apparently not emerged in the lower reaches (deltaic areas). Whether this represents lack of testing or whether arsenic problems do not occur there is as yet uncertain. However, the young Quaternary aquifers most susceptible to developing groundwater arsenic problems appear to be less used in these areas as a result of poor well vields or high groundwater salinity. Other Quaternary sedimentary aquifers in Asia have not been investigated and so their arsenic status is unknown. Some localised groundwater arsenic problems relate to ore mineralisation and mining activity (e.g. peninsular Thailand; Madhya Pradesh, India).

One of the key hydrogeochemical advances of the last few years has been in the better understanding of the diverse mechanisms of arsenic mobilisation in groundwater, as well its derivation from different mineral sources. The most important mineral sources in aquifers are metal oxides (especially iron oxides) and sulphide minerals (especially pyrite,  $FeS_2$ ). Release of arsenic from sediments to groundwater can be initiated as a result of the development of reducing (anaerobic) conditions, leading to the desorption of arsenic from iron oxides and breakdown of the oxides themselves. Such reducing conditions are commonly found in fine-grained deltaic, alluvial and lacustrine sediments.

Release of arsenic can also occur in groundwaters with high pH (>8) in oxidising (aerobic) conditions. These tend to occur in arid and semi-arid settings with pH increases resulting from extensive mineral reaction and evaporation. High-arsenic groundwaters with this type of association have not been reported in Quaternary aquifers in South and East Asia but are found in some arid inland basins in the Americas (western USA, Mexico, Argentina). Analogous conditions could occur in some arid parts of the region such as northern China or western Pakistan but there is as yet no evidence for this.

Mobilisation of arsenic in mineralised and mining areas is linked to the oxidation of sulphide minerals. Here, occurrences can affect both surface waters and groundwaters but the affected areas are typically localised (a few kilometres around the mineralised zone) as a result of the normally strong capacity of soils and aerobic sediments to adsorb arsenic.

Despite this improved understanding of the occurrences and distribution of arsenic in groundwater, there remains much uncertainty in the nature of the source, mobilisation and transport of the element in aquifers. It is only in the last few years that detailed hydrogeochemical investigations have been carried out in affected regions. Earlier responses to water-related arsenic problems typically involved engineering solutions or finding alternative water sources, with little emphasis on research. It is worthy of note that, despite the major epidemiological investigations that have been carried out in Taiwan since the discovery of arsenic-related problems there in the 1960s, there has been little hydrogeochemical research carried out in the region. Even today, the aquifers of Taiwan are poorly documented and the arsenic occurrence little understood.

One of the important findings of recent detailed aquifer surveys has been the large degree of spatial variability in arsenic concentrations, even over distances of a few hundred metres. This means that predictability of arsenic concentrations on a local scale is poor (and probably will always be so). Hence, blanket testing of individual wells in affected areas is necessary. This can be a major task in countries like Bangladesh where the scale of contamination is large. There is also uncertainty in the temporal variability of arsenic concentrations in groundwater as very little groundwater monitoring has been carried out. Some studies have noted unexpectedly large temporal variations over various timescales but the supporting data are often sparse and inaccessible and so these reports cannot be relied upon. More controlled monitoring of affected groundwaters is required to determine the variability both in the short (daily) and medium term (seasonally) as well as in the long term (years, decades).

The emerging arsenic problems have revealed the dangers of groundwater development without consideration of water quality in tandem with water quantity. Understanding of the risk factors involved in development of high-arsenic groundwaters has allowed targeting those aquifers perceived to be most susceptible to developing groundwater arsenic problems in recent years (e.g. Quaternary sediments in Cambodia, Myanmar, Nepal). However, the toxicity of arsenic is such that it should be also given greater attention in other aquifers used for drinking-water supply. There is an argument for routine testing for arsenic in all new wells provided in major groundwater development projects, regardless of aquifer type. Randomised reconnaissance-scale sampling for arsenic is also recommended for existing public-supply wells in all aquifer types where no arsenic data currently exist in order to obtain basic statistics on the distribution of arsenic concentrations. Groundwater development in previously unexploited but potentially vulnerable young sedimentary aquifers needs to be preceded by detailed hydrogeological and hydrochemical investigations to ensure that groundwater will be of sufficiently high and sustainable quality. The scale of investigations should be commensurate with the scale of proposed development.

# Glossary

Adsorption: adherence of a chemical or compound to a solid surface.

*Alluvial:* deposited by rivers.

Aquifer: water-bearing rock formation.

*Desorption:*....release of a chemical or compound from a solid surface (opposite of adsorption).

*Distal:* remote from the origin (e.g. sediments in lower reaches of a delta).

*Geothermal:* pertaining to the internal heat of the earth. Geothermal zones are areas of high heat flow, where hot water and/or steam issue at the earth's surface. They are found close to tectonic plate boundaries or associated with volcanic systems within plates. Heat sources for geothermal systems may be from magmatism, metamorphism or tectonic movements.

*Pyrite:* iron sulphide (FeS<sub>2</sub>), also known as fool's gold. Occurs commonly in zones of ore mineralization and in sediments in reducing conditions.

*Quaternary:* period of geological time extending from ca. 2 million years ago to the present day. Divided into the earliest period, the Pleistocene, and the subsequent Holocene (the last 13,000 years). Strata of Quaternary age are very young on a geological timescale.

*Mineralisation:* the presence of ore or non-ore minerals in host rocks, concentrated as veins, or as replacements of existing minerals or disseminated occurrences; typically gives rise to rocks with high concentrations of some of the rarer elements.

*Redox reactions:* .... coupled chemical oxidation and reduction reactions involving the exchange of electrons. Many elements have changeable redox states, in groundwater the most important redox reactions involve the oxidation or reduction of iron and manganese, introduction or consumption of nitrogen compounds (including nitrate), introduction or consumption of oxygen (including dissolved oxygen) and consumption of organic carbon.

*Reducing conditions:* anaerobic conditions, formed where nearly all of the oxygen has been consumed by reactions such as oxidation of organic matter or of sulphide; reducing conditions commonly occur in confined aquifers.

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