Towards a More Effective Operational Response

Arsenic Contamination of Groundwater in South and East Asian Countries

Volume II Technical Report

The World Bank
Environment and Social Unit - South Asia Region
Water and Sanitation Program (WSP) - South and East Asia

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Background and Introduction

i. The detrimental health effects of environmental exposure to arsenic have become increasingly clear in the last few years. High concentrations detected in groundwater from a number of aquifers across the world, including in South and East Asia, have been found responsible for health problems ranging from skin disorders to cardiovascular disease and cancer.

ii. The problem has increased greatly in recent years with the growing use of tubewells to tap groundwater for water supply and irrigation. The water delivered by these tubewells has been found in many cases to be contaminated with higher than recommended levels of arsenic. In the study region, countries affected include Bangladesh (the worst affected), India, Myanmar, Nepal, and Pakistan (South Asia); and Cambodia, China (including Taiwan), Lao People's Democratic Republic, and Vietnam (East Asia).

iii. This study concentrates on operational responses to arsenic contamination that may be of practical use to actors who invest in water infrastructure in the affected countries, including governments, donors, development banks, and nongovernmental organizations (NGOs).

Objectives and Audience of the Study

iv. The objectives of this study are (a) to take stock of current knowledge regarding the arsenic issue; and (b) to provide options for specific and balanced operational responses to the occurrence of arsenic in excess of permissible limits in groundwater in Asian countries, while taking into account the work that has already been carried out by many different stakeholders.

v. The study provides information on (a) occurrence of arsenic in groundwater; (b) health impacts of arsenic; (c) policy responses by governments and the international community; (d) technological options for and costs of arsenic mitigation; and (e) economic aspects of the assessment and development of arsenic mitigation strategies. The focus of the study is on rural rather than urban areas, due to the particular difficulties associated with applying mitigation measures in scattered rural communities.

vi. The study is structured as follows:

Volume I: Policy Report. This report summarizes the main messages of Volume II, and highlights the policy implications of arsenic mitigation.

This Volume II comprises four specialist papers:

- Paper 1. Arsenic Occurrence in Groundwater in South and East Asia: Scale, Causes, and Mitigation
- Paper 2. An Overview of Current Operational Responses to the Arsenic Issue in South and East Asia
- Paper 3. Arsenic Mitigation Technologies in South and East Asia
- Paper 4. The Economics of Arsenic Mitigation

The Scale of the Arsenic Threat

vii. In South and East Asia an estimated 60 million people are at risk from high levels of naturally-occurring arsenic in groundwater, and current data show that at least 700,000 people in the region have thus far been affected by arsenicosis. However, although the negative health effects of arsenic ingestion in general, and the specific impact of ingestion of arsenic-contaminated groundwater, have both been widely studied, there is still no clear picture of the epidemiology of arsenic in South and East Asia, and uncertainty surrounds such issues as the spatial distribution of contamination; the symptoms and health effects of arsenic-related diseases, and the timeframe over which they develop; and the impact of arsenic compared to other waterborne diseases whose effects may be more immediate.

viii. While arsenic is clearly an important public health threat, it needs to be noted that morbidity and mortality due to other waterborne diseases is also a serious health issue. Therefore, mitigation measures to combat arsenic contamination in South and East Asia need to be considered within the wider context of the supply of safe water.

ix. Due to the carcinogenic nature of arsenic, the World Health Organization (WHO) recommends a maximum permissible concentration for arsenic in drinking water of 10 µg L^{-1} (micrograms per liter), which has been adopted by most industrial countries. Most developing countries still use the former WHO-recommended concentration of 50 µg L^{-1} as their national standard, due to economic considerations and the lack of tools and techniques to measure accurately at lower concentrations. Further studies are needed to assess the relationship between levels of arsenic and health risks in order to quantify the inevitable trade-offs at different standards between such considerations as health risks, the ability of people to pay for safe water, and the availability of water treatment technology.

Distribution of Arsenic Contamination

x. The concentration of arsenic in natural waters globally, including groundwater, is usually below the WHO guideline value of 10 µg L^{-1}. However, arsenic mobilization in water is favored under reducing (anaerobic) conditions, leading to the desorption of arsenic from iron (and other metal) oxides. In South and East Asia such conditions tend to occur in shallow aquifers in Quaternary strata underlying the region's large alluvial and deltaic plains (Bengal basin, Irrawaddy delta, Mekong valley, Red River delta, Indus plain, Yellow River plain). (Some localized groundwater arsenic problems relate to ore mineralization and mining activity, which are not the focus of this study.) Recent hydrogeochemical investigations have improved our knowledge of the occurrence and distribution of arsenic in groundwater, though much uncertainty remains regarding the source, mobilization, and transport of the element in aquifers.

xi. 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 meters. Temporal variability also occurs, though insufficient monitoring has been carried out to establish a clear picture of variations in arsenic levels over different timescales.

Arsenic Mitigation Measures

xii. Arsenic mitigation requires a sequence of practical steps involving enquiry and associated action. Assessing the scale of the problem (now and over time) involves field testing, laboratory testing, and monitoring; identifying appropriate mitigation strategies involves technological, economic, and sociocultural analysis of possible responses; and implementation involves awareness raising and direct action by governments, donors, NGOs, and other stakeholders at local, national, and regional levels. Sustainability in the long run remains a major challenge.

xiii. The two main technological options for arsenic mitigation are (a) switch to alternative, arsenic-free water sources; or (b) remove arsenic from the groundwater source. Alternatives in the first category include development of arsenic-free aquifers, use of surface water and rainwater harvesting; alternatives in the second category involve household-level or community-level arsenic removal technologies. For each option there will be a wide range of design specifications and associated costs.

xiv.   Despite continuing uncertainty regarding arsenic occurrence and epidemiology, the lethal nature and now well-established effects of arsenic exposure in South and East Asia make it necessary that informed choices and trade-off decisions are made to address arsenic contamination of drinking water sources and the scope and extent of mitigation measures, within the context of the development of the water sector and the wider economy.

xv.   Accordingly, a simple cost-benefit methodology has been developed that takes into account data limitations and provides decisionmakers with an approach for rapid assessment of the socioeconomic desirability of different mitigation policies under various scenarios. In particular, the methodology permits an analysis of options in order to choose between different approaches in dealing with (a) the risk that arsenic might be found in an area where a project is planned; and (b) the risk mitigation options where a project's goal is arsenic mitigation per se.

xvi.   Demand-side perspectives are an important consideration for designing arsenic mitigation measures that meet the requirements of households and communities. For example, are users willing to pay for an alternative such as piped water? Demand preferences can be assessed through contingent valuation or willingness to pay studies and can provide important guidance to decisionmakers. There is a need to strengthen institutional capacities in the countries to carry out such assessments.

The Political Environment of Arsenic Mitigation

xvii.   Arsenic has become a highly politicized topic in the international development community and within some affected countries due to its carcinogenic characteristics and due to the earlier failure to consider it as a possible natural contaminant in groundwater sources. This factor makes rational analysis of the issue difficult and highlights the fact that application of mitigation measures needs to consider the political as well as the social and economic climate. The scattered rural communities most affected by arsenic contamination often have limited political presence and are in particular need of support.

xviii.   Governments that want to address the arsenic issue will therefore have to take a stronger lead role in their countries and on the international plane. This goes both for more strategic research and knowledge acquisition regarding arsenic in their countries, as well as for the choice and scope of arsenic mitigation activities.

The Importance of an Effective Operational and Strategic Approach

xix.   Significant strides have been made since arsenic was first detected in drinking water tubewells in Eastern India and Bangladesh in the late 1980s and early 1990s. However, a range of factors — including projected population growth in the region, continuing private investment in shallow tubewells, and the drive towards achievement of the Millennium Development Goal related to safe water supply — add to the urgency of adopting a more strategic approach for effective action at project, national, and international levels.

xx.   At project level, any interventions that consider using groundwater as a source must involve an assessment of whether occurrence of arsenic would affect the outcome of the project. Such an assessment would include consideration of technical factors (such as screening and possible mitigation technologies), social and cultural factors, and economic factors (including a cost-benefit or least-cost analysis).

xxi.   Some countries have taken arsenic to the national level of attention, including Bangladesh, Nepal, and Cambodia. Others, such as India, Pakistan, and China, have only started to address the issue, while in other international organizations such as UNICEF and local NGOs and universities are the focal points for arsenic-related activities. Although the characteristics of arsenic contamination are unique to each affected country, study results suggest that three simple steps would help governments more effectively address the problem now and in the future: (a) encourage further research in potentially arsenic-affected areas in order to better determine the extent of the problem; (b) ensure that arsenic is included as a potential risk factor in decision-making about water-related issues; and (c) develop options for populations in known arsenic-affected areas.

xxii.   At the global level, focused research on the chemistry of arsenic mobilization and the dose-response relationships for arsenic are of vital importance in formulating a more effective approach. If governments and the international community are to achieve the MDGs in water supply and sanitation then the knowledge gaps regarding arsenic need to be filled, notably by (a) further epidemiological research directly benefiting arsenic-affected countries; (b) socioeconomic research on the effects of arsenicosis, understanding behavior and designing demand-based packages for the various arsenic mitigation techniques; and (c) hydrogeological and hydrochemical research.

xxiii.   It also needs to be made clear that, due to the nature of arsenic itself, in the not-so-distant future there will be diminishing returns on investments in scientific arsenic research to reduce uncertainty. The important challenge will be to identify those areas where improved research-level data collection is likely to provide a major return. For other areas the main question will be how to manage in the face of unavoidable and continuing uncertainty.

xxiv.   Accordingly, the international dialogue should shift towards targeted research priorities that address these issues. This would also include the pursuit of the research agenda regarding arsenic in the food chain. Both the World Bank and a number of development partners are contributors to the Consultative Group on International Agricultural Research (CGIAR) and this organization would lend itself to building up a coherent and focused research agenda on this topic in order to provide decisionmakers with guidance regarding arsenic-contaminated groundwater.

Abbreviations and Acronyms

The following list includes all abbreviations and acronyms used throughout Volumes I and II of the report.

AAN	Asian Arsenic Network
AAS	atomic absorption spectrometer/spectrometry
AES	atomic emission spectrometry
AIIH&PH	All India Institute of Hygiene and Public Health
APSU	Arsenic Policy Support Unit (Bangladesh)
As	arsenic
ASV	anodic stripping voltammetry
AusAID	Australian Agency for International Development
AWWA	American Water Works Association
BAMWSP	Bangladesh Arsenic Mitigation Water Supply Project
BGS	British Geological Survey
BUET	Bangladesh University of Engineering and Technology
CBA	cost-benefit analysis
CCA	chromated copper arsenate
CEPIS	Pan American Center for Sanitary Engineering and Environmental Sciences (Peru)
CGIAR	Consultative Group on International Agricultural Research
Danida	Danish Agency for International Development
DF	discount factor
DOC	dissolved organic carbon
DPHE	Department of Public Health Engineering (Bangladesh)
DWSS	Department of Water Supply and Sewerage (Nepal)
EAWAG	Swiss Federal Institute for Environmental Science and Technology
EPA	Environmental Protection Agency (United States)
GDP	gross domestic product
GF-AAS	graphite furnace-atomic absorption spectrometry
GPL	General Pharmaceutical Ltd.
GPS	global positioning system
GWMATE	World Bank Groundwater Management Advisory Team
HG-AAS	hydride generation-atomic absorption spectrometry
HG-AFS	hydride generation-atomic fluorescence spectrometry
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma-mass spectrometry
IRC	International Water and Sanitation Center (formerly International Reference Center for Community Water Supply)
JICA	Japan International Cooperation Agency
Lao PDR	Lao People's Democratic Republic
MDG	Millennium Development Goal
MS	mass spectrometry
NAMIC	National Arsenic Mitigation Information Center (Bangladesh)
NASC	National Arsenic Steering Committee (Nepal)
NGO	nongovernmental organization
NPV	net present value
NRC	National Research Council (United States)
NRCS	Nepal Red Cross Society
NTU	nephelometric turbidity unit
PAHO	Pan American Health Organization
PV	present value
SDDC	silver diethyldithiocarbamate
SORAS	solar oxidation and removal of arsenic
TCLP	toxic characteristic leaching procedure
UNCHS	United Nations Centre for Human Settlements
UNDP	United Nations Development Program
UNICEF	United Nations Children's Fund
WHO	World Health Organization
WRUD	Water Resources Utilization Department (Myanmar)

Units of Measurement

µg	microgram
mg	milligram
kg	kilogram
L	liter
µg L^{-1}	micrograms per liter
mg L^{-1}	milligrams per liter
cm	centimeter
m	meter
km	kilometer

Units of Currency (January 2004)

1 US$ = 58 taka (Tk) (Bangladesh)
1 US$ = 48 rupees (Rs) (India)

Paper I

Arsenic Occurence in Groundwater in South and East Asia

– Scale, Causes, and Mitigation

Prepared by Dr. Pauline Smedley, British Geological Survey

Acknowledgments

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 detected 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 World Health Organization (WHO) provisional guideline value for arsenic in drinking water of 10 µg L^{-1}. However, arsenic mobilization in water is favored 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 mobilization occurs in sedimentary aquifers are still not well understood. However, the development of reducing (anaerobic) conditions in the aquifers has been recognized 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, oxidizing (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 high-arsenic aquifers do not contain unusually high arsenic concentrations. Typical concentrations are of the order of 5–10 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 unrecognized problems on such a large scale as that identified in the Bengal basin is not impossible but is considered unlikely.

6.   Mineralized 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 kilometers around the mineralized 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 recognized arsenic-affected areas. Despite common associations between arsenic and a number of other trace elements (for example 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 oxidizing conditions that pertain in most surface environments. Under oxidizing conditions, adsorption of arsenic to sediments and soils occurs and mobilization in soluble form is not favored. 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 their 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 oxidizing, comprising a high proportion of freshly recharged rainwater and being open to the atmosphere. Most groundwater samples analyzed from dug wells in Bangladesh, West Bengal, Myanmar, and Nepal have been found to

contain arsenic concentrations less than 50 μg L^{-1} (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 μg L^{-1} have been found in groundwater from dug wells in a number of the recognized 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 of up to 560 μg L^{-1} have been found in dug well water from Inner Mongolia (China) where anaerobic conditions have been maintained in low-lying areas of groundwater discharge that are characterized 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 μg L^{-1}) has been found in, for example, 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 meters) 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 over their geological history than the sediments bearing high-arsenic 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 mobilization. Rather, dissolved arsenic concentrations are determined by a combination of geochemical conditions suitable for mobilizing 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 a prerequisite to groundwater development.

15.   On a regional scale, our understanding of arsenic mobilization 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. Randomized reconnaissance groundwater arsenic surveys of such areas are the logical first step in identifying problem areas, followed 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 prioritization, 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 programs. Such programs 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 μg L^{-1} and 46% have concentrations greater than 10 μg L^{-1}. 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 over-reactive to abandon groundwater in favor of alternatives without first carrying out testing programs 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 characterizes 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.

1. Introduction

Pathways of Arsenic Exposure

The dangers associated with long-term exposure to arsenic are now well known. 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 often constitute the most reliable sources of safe drinking water. Groundwater is also less vulnerable to contamination from the waterborne 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 than in stems, leaves, or economic produce. However, few results have been published so far. Meharg and Rahman (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^{-1} (compared, for example, with the 1 mg kg^{-1} Australian standard for inorganic arsenic in food). However, few samples were analyzed and the values found are higher than those in other studies of naturally cultivated rice carried out to date (Abedin, Cotter-Howells, and Meharg 2002). The bioavailability of arsenic in rice is also uncertain and is 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 2002). 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 of rice, could become an important issue (Abedin and Meharg, 2002).

Arsenic-contaminated air is also a potential exposure pathway in some cases. In Guizhou Province, southern China, severe chronic health problems have arisen from the burning of local coal with very high arsenic concentrations (up to 35,000 mg kg^{-1}), the exposure being both by inhalation and consumption of chillis dried over domestic coal fires (Finkelman, Belkin, and Zheng 1999). This pathway is much more localized than that from drinking water but, in China, an estimated 3,000 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 been reduced in recent years following increased evidence of its toxic effects to humans. The World Health Organization (WHO) guideline value was reduced from 50 µg L^{-1} to 10 µg L^{-1} in 1993 although the recommendation is still provisional pending further scientific evidence. 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 and Vietnam) remain at 50 µg 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 less than the WHO guideline value of 10 µg L^{-1} and commonly below analytical detection limits. An investigation of some 17,500 groundwater samples from public supply wells in the United States of America, for example, found that 7.6% exceeded 10 µg L^{-1} and 1% exceeded 50 µg L^{-1}, while 64% contained <1 µg L^{-1} (Focazio and others 1999). Despite the usually low abundance in water, high concentrations can occur in some groundwaters. Under geochemically and hydrogeologically favorable conditions concentrations can reach tens to hundreds of µg L^{-1} and, in a few cases, can exceed 1 mg L^{-1}.

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 sulfide and oxide minerals, especially iron sulfides and iron oxides. As a result, high arsenic concentrations in water are often found where these minerals are in abundance. Mineralized areas are well-documented examples. These contain ore minerals, including sulfide minerals, typically as veins or replacements of original host rocks and result from past infiltration of hydrothermal fluids. In mineralized 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 mineralization 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 scale of contamination is usually not of large lateral extent. This is due to the normally strong adsorption capacity of iron oxides, which leads to removal of arsenic and other potentially toxic trace elements from water.

Despite these associations, other areas with recognized high-arsenic groundwaters are not associated with obvious mineralization 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, southwest United States, Hungary, Romania, Bangladesh, India, China (including Taiwan), Myanmar, Nepal, 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 semiarid settings (for example Argentina, Mexico, southwest United States) or large alluvial and deltaic plains (for example 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 favorable for mobilization and retention in solution.

Figure 1. Summary of the World Distribution of Documented Problems with Arsenic in Groundwater and the Environment

Source: Modified after Smedley and Kinniburgh 2002.
Note: In China, arsenic has further been identified in the provinces of Jilin, Qinghai, Anhui, Beijing, and Ningxia (reported at Regional Operational Responses to Arsenic Workshop in Nepal, 26–27 April 2004).
In India, further affected states are Assam, Arunachal Pradesh, Bihar, Manipur, Meghalaya, Nagaland, Uttar Pradesh and Tripura.

2. Arsenic Distribution in South and East Asia

Overview

Many of the world's aquifers with recognized arsenic problems are located in Asia where large alluvial and deltaic plains occur, particularly around the perimeter of the Himalayan mountain range (figure 2). 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,

Figure 2. Map of South and East Asia Showing the Locations of Documented High-Arsenic Groundwater Provinces
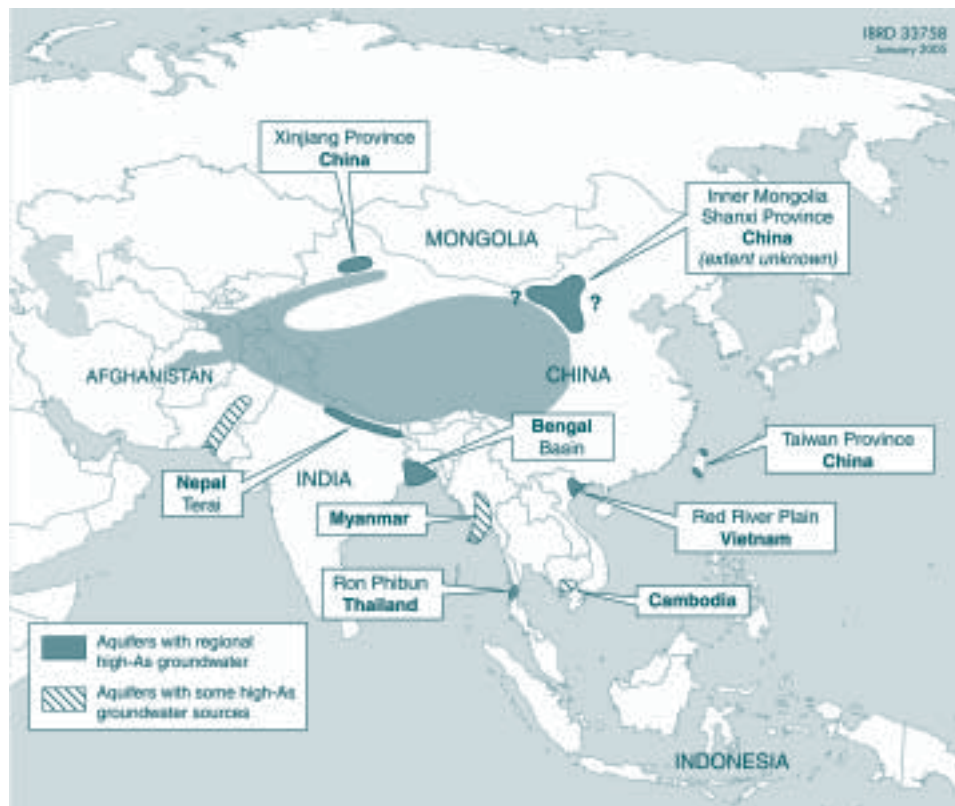
Source: Modified after Smedley 2003.

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 recognized occurrences, aquifers involved, and populations potentially at risk (that is, using drinking water with arsenic concentrations >50 μg L^{-1}) is given in table 1. Some of these population statistics are poorly constrained given the present state of knowledge.

Box 1. Analysis of Arsenic

Arsenic is a trace element that is present at μg L^{-1} concentrations in most natural waters. Sampling and analyzing 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 program to ensure that data produced are of good quality throughout the program. This includes adequate record-keeping, sample tracking, regular use of analytical standards, interlaboratory (round robin) checks, and duplicate analyses.

The most precise and sensitive analytical methods depend on sophisticated laboratory instruments such as hydride generation-atomic absorption spectrometry (HG-AAS), inductively coupled plasma-mass spectrometry (ICP-MS), and hydride generation-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 US$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 multielement techniques and so provide information on elements other than arsenic. There are cheaper and more robust instruments, such as that employed by the silver diethyldithiocarbamate (SDDC) method, but these are less sensitive, are slow, and may not be appropriate for large screening programs. 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 US$1 per sample for the materials. The early kits were insufficiently sensitive (being barely capable of detecting less than 100 μg L^{-1}). However, they have improved in the last few years and the best can now detect down to 10 μg L^{-1}, the WHO guideline value. In practice, the reproducibility of the kits has often proven disappointing and care has to be taken to ensure that good results are obtained consistently during a survey (Rahman and others 2002).

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 minimize their impact, for example by reanalyzing samples that are very different from those taken from neighboring 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.

Alluvial, Deltaic, and Lacustrine Plains

Bangladesh

Of the regions of the world with groundwater arsenic problems Bangladesh is the worst case identified, with some 35 million people thought to be drinking groundwater containing arsenic at concentrations greater than 50 µg L^{-1} (table 1) and around 57 million drinking water with concentrations greater than 10 µg L^{-1} (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. The Bangladesh Department of Public Health Engineering (DPHE) and the United Nations Children's Fund (UNICEF) carried out surveys of

Table 1. Summary of the Distribution, Nature, and Scale of Documented Arsenic Problems (>50 µg L^{-1}) in Aquifers in South and East Asia

Location	Areal extent (km²)	Population at risk[a]	Arsenic range (µg L^{-1})
Alluvial/deltaic/ lacustrine plains			
Bangladesh	150,000	35,000,000	<1-2,300
China (Inner Mongolia, Xinjiang, Shanxi)	68,000	5,600,000	40-4,400
India (West Bengal)	23,000	5,000,000	<10-3,200
Nepal	30,000	550,000	<10-200
Taiwan (China)	6,000	(?) 10,000[b]	10-1,800
Vietnam	1,000	10,000,000[c]	1-3,100
Myanmar	(?) 3,000	3,400,000	-
Cambodia	(?) <1,000	320,000[d]	-
Pakistan	-	-	-

- Not available.
[a] Estimated to be drinking water with arsenic >50 µg L^{-1}. From Smedley 2003 and data sources therein.
[b] Before mitigation.
[c] United Nations Children's Fund (UNICEF) estimate.
[d] Maximum.
Source: World Bank Regional Operational Responses to Arsenic Workshop in Nepal, 26-27 April 2004.

51,000 wells during 1997-1999 using arsenic field test kits. The British Geological Survey (BGS) and the DPHE conducted a survey of around 3,500 samples nationwide during 1998-1999 (BGS and DPHE 2001). Over the last few years, the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) and a number of nongovernmental organizations (NGOs) and international agencies (for example the Japan International Cooperation Agency (JICA), the Asian Arsenic Network (AAN), NGO Forum, UNICEF, World Vision International, and Watsan Partnership) have carried out major screening programs of groundwaters across Bangladesh. Van Geen, Zheng, and others (2003) also analyzed samples from about 6,000 wells in eastern Bangladesh. To date more than 4.2 million tubewells have been tested for arsenic. However, this is still only around 39% 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 2,300 µg L^{-1}, though concentrations span more than four orders of magnitude (BGS and DPHE 2001). Van Geen, Zheng, and others (2003) found concentrations in the range <5-860 µg L^{-1} 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 southeast 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 µg L^{-1}. Some areas with low overall arsenic concentrations have localized hotspots with locally high arsenic concentrations. That of the Chapai Nawabganj area of western Bangladesh is a notable example (figure 4 see page 34), where the median concentration in groundwater from Holocene sediments was found to be 3.9 µg L^{-1} but with extremes up to 2,300 µg 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 µg L^{-1} and 46% exceeded 10 µg L^{-1}.

Figure 3. Smoothed Map of Arsenic Distribution in Groundwater from Bangladesh
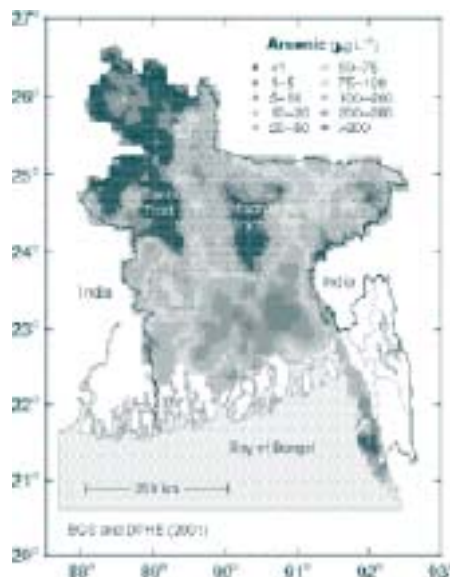
Note: Samples are from tubewells <150 m deep.
Source: BGS and DPHE 2001.

Figure 4. Maps of the Distribution of Arsenic in Shallow Groundwater from the Chapai Nawabganj Area, Northwest Bangladesh
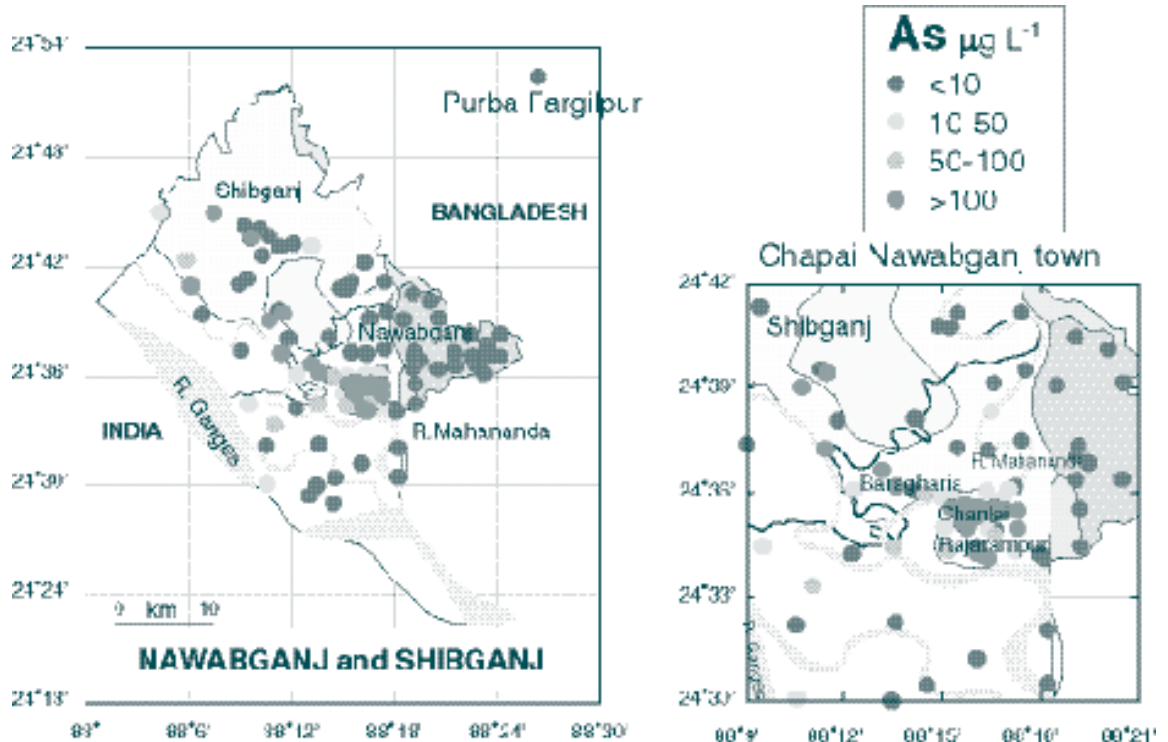
Note: Samples are from tubewells <150 m deep
Source: BGS and DPHE 2001.

Investigation of the depth ranges of affected tubewells suggests that concentrations are low in groundwater from the top few meters 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 groundwater compositions in a piezometer (10 cm diameter, 40 m deep) in Chapai Nawabganj, northwest Bangladesh. Arsenic concentration was relatively low (17 µg L^{-1}) at 10 m depth but increased to values in the range 330-400 µg L^{-1} 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 analyzed 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 mg L^{-1} and concentrations of uranium are also sometimes high (up to 32 µg L^{-1}). Concentrations of boron exceed WHO guidelines in some saline groundwaters from the south and east of Bangladesh.

Figure 5. Variation in Concentration of Arsenic and Other Elements with Depth in a Purpose-Drilled Piezometer in Chapai Nawabganj, Northwest Bangladesh
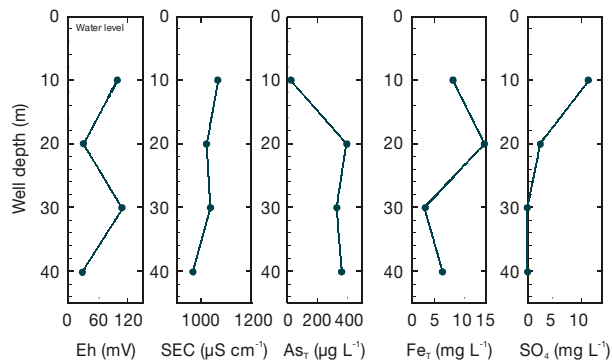
Source: BGS and DPHE 2001.

Table 2. Frequency Distribution of Arsenic in Groundwater from Tubewells from Quaternary Alluvial Aquifers in Bangladesh

Tubewell depth range (m)[a]	Number of samples (%)			Total samples
	<10 µg L^{-1}	10-50 µg L^{-1}	>50 µg L^{-1}	
<25	597 (53)	193 (17)	327 (30)	1,117
25-50	740 (57)	211 (16)	354 (27)	1,305
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

[a] Depth of intake of groundwater is difficult to determine and may be from several horizons at differing depths.
Source: BGS and DPHE 2001.

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 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 µg L^{-1} and often significantly less. Similar results for these areas have also been obtained by other workers (for example van Geen, Zheng, and others 2003).

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, Zheng, and others 2003). Limited investigations indicate that they are mineralogically distinct from the overlying Holocene deposits. They are typically more brown in color and relatively oxidized. The deep aquifer sediments are likely to be akin to the aquifers below the Barind and Madhupur tracts, which occur at shallower depths because 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 organizations 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 the BAMWSP for groundwater samples from 60 upazilas across Bangladesh found that out of 7,123 samples from tubewells >150 m deep, 97% had arsenic concentrations <50 μg L^{-1} (percentage <10 μg L^{-1} unspecified; BAMWSP website). The

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 μg L^{-1}. The depth at which these deep aquifers occur varies but is typically more than 100–150 m below surface. Deep aquifers have been tapped in southern coastal areas and northeastern 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 increased 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 μg 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 characterized. 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.

BGS and DPHE (2001) national survey categorized shallow aquifers as those less than <150 m depth and deep aquifers as >150 m. Of 335 samples analyzed from >150 m depth, 95% were found to have arsenic concentrations <10 µg L^{-1} (table 2). Most of the deep groundwater samples analyzed in the BGS and DPHE survey were from the southern coastal area (Barisal) and the northeast (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 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 µg L^{-1} (five 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, Zheng, and others (2003) 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 varies in different parts of Bangladesh and it is not possible to define the depth at which low-arsenic 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 analyzed 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 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 µg L^{-1}, with most being <10 µg L^{-1} (for example Chakroborti 2001). BGS and DPHE (2001) found concentrations in five dug wells from north-west Bangladesh (Chapai Nawabganj) in the range <3-14 µg L^{1} , with a median of 7.6 µg L^{-1}. Two samples exceeded 10 µg 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 µg L^{-1}, manganese up to 1.7 mg L^{-1} , and nitrate-N up to

Box 3. Dug Wells

Concentrations of arsenic in dug wells are often low, even in areas where those in groundwater from neighboring tubewells are high. In western Bangladesh, a 30 m deep tubewell with a groundwater arsenic concentration of around 2,300 µg L^{-1} is located just a few meters from an 8 m deep dug well with an arsenic concentration of less than 4 µg L^{-1}. Groundwater in the top few meters 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 µg 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 µg 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 handpump 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 handpumped tubewells as a means of obtaining improved yields and sanitary protection. Nonetheless, they are still used by significant numbers of people, and in some areas 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.

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.

Bengal Delta and Associated Aquifers, India

Problems with arsenic in groundwater in West Bengal were first recognized in the late 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 µg L^{-1} (table 1). More recently, problems have also been found in Arunachal Pradesh, Assam, Bihar, Nagaland, Manipur, Meghalaya, Tripura, and Uttar Pradesh. The state of Mizoram also has important Quaternary sedimentary aquifers that 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 µg L^{-1} and 20% exceeded 300 µg L^{-1}. Concentrations were up to 1,650 µg L^{-1} (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 problem 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 see page 40). These cover around 23,000 km^2 to the east of the Bhagirathi-Hoogli river system. Arsenic concentrations have been found in the range <10-3,200 µg 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).

Figure 6. Map of West Bengal Showing Districts Affected by High Groundwater Arsenic Concentrations

Note: Numbers refer to number of blocks with arsenic concentrations >50 μg L⁻¹ relative to total number of blocks. Darker shading shows worst-affected areas (data as of 1999).

The Quaternary sediments have a similar configuration to those of Bangladesh but the aquifers have been categorized 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 that is oxidized 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 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 μg L⁻¹) 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 800,000 tubewells, which supply groundwater for some 11 million people (World Bank Regional Operational Responses to Arsenic Workshop, Nepal, 26–27 April 2004). About 15% 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 abstract 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 intermontane basins in Nepal, most notably that of the Kathmandu valley of central Nepal (ca. 500 km^2), 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 analyzed appear to have <10 µg L^{-1}. Arsenic-related health problems have been detected in some of the affected areas. Water analyses have mostly been determined (using 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 were 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 µg L^{-1}, while 31% exceeded 10 µg L^{-1}, and 8% exceeded 50 µg L^{-1} (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 central and western Terai. The highest concentration observed (Rupandehi District) was 2,600 µg L^{-1} (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 4,000 tubewells from the 20 Terai districts, mostly analyzed 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 µg L^{-1} (Chitrakar and Neku 2001). The highest observed concentration was 343 µg L^{-1} (Parsa District). From testing in

Table 3. Frequency Distribution of Arsenic Concentrations in Analyzed Groundwater Samples from Nepal

Agency	Number of samples (%)			Total samples
	<10 µg L^{-1}	10-50 µg L^{-1}	>50 µg L^{-1}	
DWSS	3,479 (89.3)	289 (7.3)	128 (3.3)	3,896
NRCS	2,206 (79)	507 (18)	77 (3)	2,790
Finnida	55 (71)	14 (18)	9 (12)	78
Tandukar	54 (61)	27 (30)	8 (9)	89
NASC (2003)	17,300 (69)	6,000 (23)	2,000 (8)	25,000

Sources: Chitrakar and Neku 2001; Tandukar 2001; Neku and Tandukar 2003.

17 of the 20 Terai districts, the Nepal Red Cross Society (NRCS) also found 3% of groundwater sources sampled having concentrations above 50 µg L^{-1}, the highest observed concentration being 205 µg L^{-1}. 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 analyzed samples exceeding 50 µg L^{-1}, 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 µg L^{-1}, 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 exceeding 50 µg L^{-1} is generally small and much lower than the percentage observed in, for example, Bangladesh, but the statistics nonetheless indicate a clear requirement for further testing and remedial action. To date, there has been no substantial mitigation program in the region (Tuinhof and Nanni 2003).

Surveys appear to indicate that deeper tubewells in the Terai region 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 µg 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. Little testing for arsenic in groundwater has been carried out in tubewells from the alluvial aquifer, though a few reconnaissance surveys have been undertaken and arsenic has been found in excess of 50 µg L^{-1} in some. Save The Children reported from analysis of 1,912 shallow tubewells in four townships in Ayeyarwaddy Division (southern delta area) that 22% of samples exceeded 50 µg L^{-1}. The United Nations Development Programme (UNDP) and the United Nations Centre for Human Settlements (UNCHS) detected arsenic at concentrations greater than 50 µg L^{-1} in 4% of samples (125 samples) from Nyaungshwe in Shan State in southern Myanmar (UNDP-UNCHS 2001). The Water Resources Utilization Department (WRUD) carried out a survey of groundwater in Sittway township in the western coastal area, and in 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, although some deeper tubewells (55–70 m) were also sampled. In the southern townships of the delta area, high iron concentrations were noted. The distribution of arsenic concentrations determined by 2001 is given in table 4. Exceedances above 50 µg L^{-1} 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 µg L^{-1}. As with a number of other affected aquifers, dug wells from the WRUD survey generally had arsenic concentrations of <10 µg L^{-1} (WRUD 2001).

Table 4. Frequency Distribution of Arsenic Concentrations in Groundwaters from the Alluvial Aquifer of Myanmar

Township	Well type	Number of samples (%)			Total samples
		<10 µg L^{-1}	10–50 µg L^{-1}	>50 µg L^{-1}	
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

Key:
STW   shallow tubewell
DW   dug well
DTW   deep tubewell (55–70 m)
Source: WRUD 2001.

More recent results from WRUD surveys have shown 15% of groundwater samples exceeding 50 µg L^{-1} (8,937 analyses by April 2002). In these, dug wells were found to exceed 50 µg L^{-1} 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 of Ayeyarwaddy and Bago (delta area), and the states of Mon and Shan, appear to be the worst affected.

Quaternary Aquifers, Taiwan, China

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. Taiwan is the classic area for the identification of blackfoot disease (for example 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 over the last 40 years or so, 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 recognized in two areas: the southwest coastal area (Kuo 1968; Tseng and others 1968) and the northeast coast (Hsu, Froines, and Chen 1997). Kuo (1968) observed arsenic concentrations in groundwater samples from southwest Taiwan ranging between 10 µg L^{-1} and 1,800 µg L^{-1} (mean 500 µg L^{-1}, n = 126), with half the samples analyzed having concentrations of 400–700 µg L^{-1}. 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 µg L^{-1}, with 58 townships having >350 µg L^{-1} (Lo, Hsen, and Lin 1977). In northeastern Taiwan Hsu, Froines, and Chen (1997) reported an average arsenic concentration of 135 µg L^{-1} for 377 groundwater samples.

In the southwest, 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 as well as humic substances (Tseng and others 1968). Groundwaters abstracted in northeastern Taiwan are also reported to be artesian but more typically shallow, with a depth range of 16–40 m (Hsu, Froines, and Chen 1997). As found in several other countries, groundwater from shallow dug wells have low arsenic concentrations (Guo, Chen, and Greene 1994). This is probably a reflection of relatively oxidizing conditions in the shallow parts of the aquifer immediately around the open wells.

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 recognized 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 Xinjiang Province and more recently in parts of Inner Mongolia and Shanxi Province (figure 7). Concentrations of arsenic up to 4,400 µg L^{-1} have been found in groundwater from these affected areas. These areas represent large internal drainage basins in arid and semiarid settings. Groundwater conditions in the arsenic-affected areas appear to be strongly reducing. High-arsenic drinking water has also been identified in parts of Liaoning, Jilin, and Ningxia Provinces in northeast 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 or defined. The population exposed to drinking water with concentrations in excess of 50 µg L^{-1} (the Chinese standard) has been estimated as around 5.6 million (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 recognized in Xinjiang Province of northwest China (figure 7). The region is arid with an average annual

Figure 7. Map of China Showing the Distribution of Recognized High-Arsenic (>50 µg L^{-1}) Groundwaters and the Locations of Quaternary Sediments
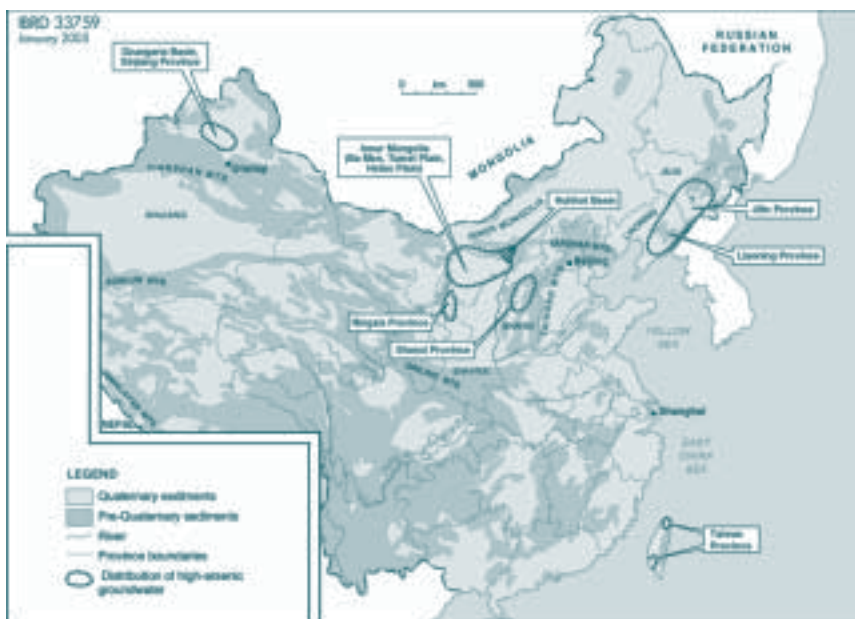
Source: Modified after Smedley and others 2003.

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 1,200 µg L^{-1} in groundwaters from the province. Wang and Huang (1994) found concentrations of between 40 µg L^{-1} and 750 µg L^{-1} in deep artesian groundwater from the Dzungaria basin on the north side of the Tianshan Mountains (up to 3,800 m 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 Quaternary 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 µg L^{-1} and 68 µg L^{-1} (average 18 µg L^{-1}). That in the saline Aibi Lake was reported as 175 µg L^{-1}, while local rivers had concentrations between 10 µg L^{-1} and 30 µg L^{-1}.

Wang and others (1997) reported arsenic concentrations up to 880 µg L^{-1} from tubewells from the Kuitan area of Xinjiang. A 1982 survey of 619 wells showed 102 with concentrations of arsenic >50 µg L^{-1}. High fluoride concentrations were also noted in the groundwaters (up to 21.5 mg L^{-1}).

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 µg L^{-1} in 837 (35%) of 2,373 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 µg L^{-1} (Sun and others 2001).

Yellow River Plain, Inner Mongolia
In Inner Mongolia, concentrations of arsenic in excess of 50 µg L^{-1} have been identified in groundwaters from aquifers in the Hetao plain, Ba Men region, and in the Tumet plain, which includes the Huhhot basin (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 µg L^{-1} (Ma and others 1999). Arsenic-related health problems from the use of groundwater for drinking were first recognized in the region in 1990 (Luo and others 1997). The most common manifestations of disease are skin lesions (melanosis, keratosis) but an increased 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 µg L^{-1}. Around 1,500 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 analyzed had arsenic concentrations greater than 50 µg L^{-1}. 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 1,350 µg L^{-1}.

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 50-1,800 µg L^{-1} (Ma and others 1999) and around 30% of wells sampled had arsenic concentrations >50 µg L^{-1}. The groundwaters are reducing with arsenic being dominantly 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 x 60 km) lies to the east of the 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 1,500 m) of poorly consolidated sediments, largely of Quaternary age (Smedley and others 2003).

Figure 8. Regional Distribution of Arsenic in Groundwaters from the Shallow and Deep Aquifers of the Huhhot Basin
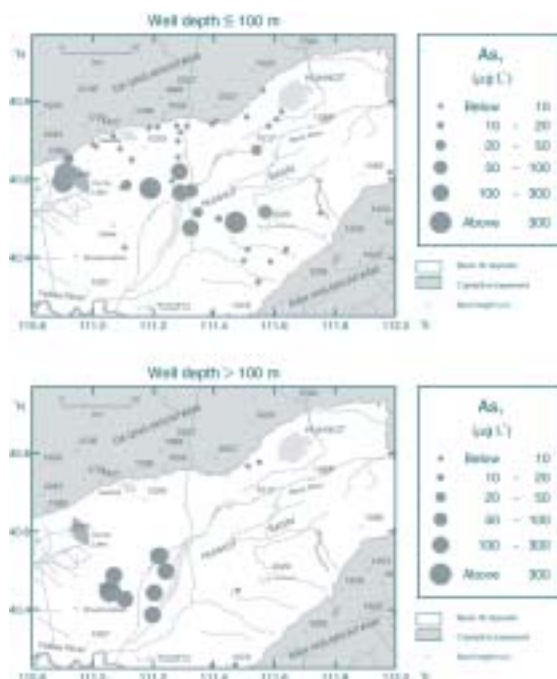
Source: Smedley and others 2003.

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 favor of tubewells that abstract at shallow levels (typically <30 m) by handpumps or in some cases by motorized 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 1,480 µg L^{-1} in the shallow aquifer (£100 m) and between <1 and 308 µg L^{-1} in the deep aquifer (>100 m). Of a total of 73 samples, summarized by Smedley and others (2003), 25% of shallow sources and 57% of deep sources have arsenic concentrations in excess of 50 µg L^{-1} (table 5 see page 48). The

Table 5. Frequency Distribution of Arsenic Concentrations in Groundwater from the Huhhot Basin, Inner Mongolia

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

Source: Smedley and others 2003.

Table 6. Summary Arsenic Data for Groundwater from Dug Wells in the High-Arsenic Groundwater Region of the Huhhot Basin

Sample	Water level m	Well depth m	DOC mg L^{-1}	Arsenic µg 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

- Not available.

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 (table 6) (Smedley and others 2001, 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 mobilization 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 µg 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, Chen, and Greene 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^{-1}). This, together with the fact that low-lying parts of the basin are zones of groundwater discharge, rates of groundwater recharge are low, and groundwater movement is sluggish, are likely reasons for the reducing conditions and stabilization 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 unsubstantiated. The total area of the plain is around 17,000 km². Groundwater is abstracted from unconsolidated Quaternary alluvial sediments which comprise up to 150 m thickness 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 southeast of the plain (Berg and others 2001; Tong 2002).

Private tubewells have generally been installed over the last decade and these abstract water via handpumps from shallow levels in the aquifer (<45 m 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 northeast 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 1-3,050 µg L^{-1} (average 159 µg 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 1,000 km² 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 µg 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 1,228 (12.5%) in seven provinces had arsenic concentrations greater than 50 µg L^{-1}. 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 factors may include differences in sediment thickness, composition, and age, and hydraulic connection between layers. In particular, 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 mobilization 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 µg L^{-1} in the dry season than the rainy season. As the data in the case of Berg and others (2001) were not reported in relation to other parameters (for example rainfall, water level), and in the case of Tong (2002) were presented just as ranges and percentage exceedances, the variations are difficult to interpret and to verify. Subsequent monitoring by the Swiss Federal Institute for Environmental Science and Technology (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.

Table 7. Summary Arsenic Data for Groundwater from Tubewells in the Red River Plain, Vietnam, Divided into Those from the Holocene and Pleistocene Aquifers

	Number of samples (%)			Total samples
	<10 µg L^{-1}	10–50 µg L^{-1}	>50 µg 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)	1,228

Sources: Tong 2001, 2002.

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 analyzed had arsenic concentrations >10 µg L^{-1}, with observed concentrations in the range 10-500 µg L^{-1}. Exceedances above 10 µg L^{-1} 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 µg L^{-1} in two additional provinces. High iron and manganese concentrations and anaerobic conditions are common features of the groundwaters throughout the lowland areas of Cambodia.

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 summarized in table 8 (see page 52). Around 19% of samples from the Holocene aquifer were found to contain arsenic at concentrations >50 µg L^{-1}. UNICEF and other

Figure 9. Geological Map of Cambodia Showing Distribution of Potentially High-Arsenic Aquifers
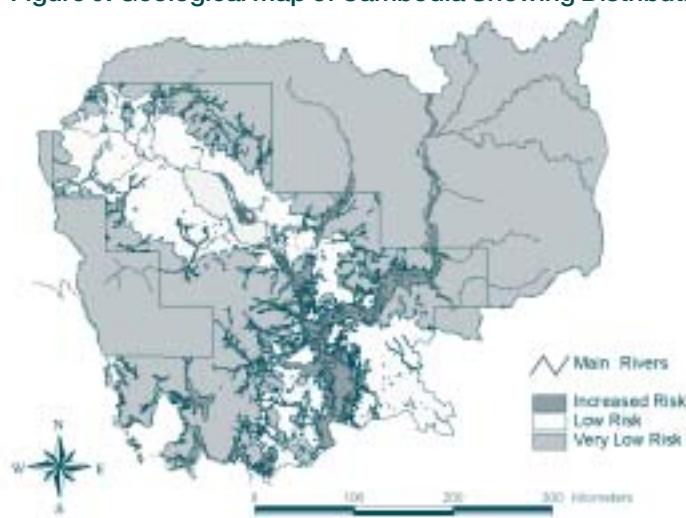
Note: Areas of perceived "increased risk" are those with aquifers of Holocene age; areas of perceived "low risk" are Pleistocene aquifers; areas of "very low risk" are crystalline basement rocks. Geological units are provisional and accuracy of national boundaries is not guaranteed. Sources: UNICEF, Cambodia; D. Fredericks, pers. comm. 2003.

Table 8. Summary Arsenic Data for Groundwater from Tubewells in the Mekong Valley of Cambodia

	Number of samples (%)			Total samples
	<10 µg L^{-1}	10–50 µg L^{-1}	>50 µg L^{-1}	
Holocene aquifer	301 (50)	185 (31)	113 (19)	599
Pleistocene aquifer	1,184 (95)	59 (5)	3 (0.2)	1,246
Crystalline rocks	708 (96)	24 (3)	2 (0.3)	734

Sources: Data from UNICEF and JICA; D. Fredericks, pers. comm., 2003.

organizations continue to support and carry out field testing using portable kits with supplementary laboratory analysis in Cambodia. A plan to blanket-test wells in 1,500 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, around Phnom Penh. Whether this reflects an impact of urbanization (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 (n.d.) provided some arsenic data measured by spectrometry for groundwater samples from the 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 µg L^{-1}. Concentrations were in the range <1–5 µg L^{-1} for groundwaters from Holocene deposits (9 samples, depth range 4–19 m), <1–32 µg L^{-1} for those from Middle and Upper Pleistocene deposits (39 samples, depth range 5–120 m), <1–7 µg L^{-1} for groundwater from Lower Pleistocene deposits (12 samples, depth range 113–191 m), and <1–57 µg L^{-1} 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 (n.d.) 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 the Attapeu, Savannakhet, Champassak, Saravan, Sekong, Khammuane, and Bolikamxay areas of Lao PDR. Results from 200 samples reported by Fengthong, Dethoudom, and Keosavanh (2002) suggested that some samples had arsenic concentrations greater than 10 µg L^{-1} but only one exceeded 50 µg L^{-1}. The highest concentration observed in the region was 112 µg L^{-1} (Attapeu Province). To date, UNICEF, in collaboration with the government and the Adventist Development and Relief Agency, have tested some 680 samples from drinking water sources and found 1% of sources having arsenic concentrations >50 µg L^{-1} (table 9, unpublished data).

Table 9. Summary Arsenic Data for Groundwater from Tubewells in the Mekong Valley of Lao PDR

	Number of samples (%)			Total samples
	<10 µg L^{-1}	10–50 µg L^{-1}	>50 µg L^{-1}	
Holocene aquifer	531 (78)	143 (21)	6 (1)	680

Source: Data from UNICEF, 2004.

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 meters 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 mobilization in groundwater should be less favorable.

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 program 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 (Gujarat). A total of 364 samples were analyzed. The majority (90%) of samples had arsenic concentrations less than 10 µg L^{-1}, although 6 samples (2%) had concentrations above 50 µg L^{-1} (table 10 see page 54) (Iqbal 2001). Further well testing for arsenic is ongoing. 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.

Table 10. Frequency Distribution of Arsenic Concentrations in Groundwater Samples from Northern Punjab

District	Number of samples (%)			Total samples
	<10 µg L^{-1}	10–50 µg L^{-1}	>50 µg L^{-1}	
Gujarat	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)	6 (8)	0 (0)	74
Rawalpindi	81 (96)	3 (4)	0 (0)	84
Total	326 (90)	30 (8)	6 (2)	364

Source: Iqbal 2001.

Mining and Mineralized 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 1). Health problems were first recognized in the area in 1987 and over 1,000 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 µg L^{-1} arsenic (Fordyce and others 1995). The affected area lies within the Southeast Asian tin belt. Primary tin-tungsten-arsenic mineralization 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 mobilization during the postmining rise in groundwater levels (Williams 1997).

Surface waters draining the bedrock and alluvial mining areas are commonly acidic (pH <6) with SO$_4$ as the dominant anion (up to 142 mg L^{-1}) and with high concentrations of some trace

metals, including aluminum (up to 10,500 µg L^{-1}), cadmium (up to 250 µg L^{-1}), and zinc (up to 4,200 µg L^{-1}) (Williams and others 1996). Strong positive correlations are observed between SO$_4$ and cadmium, aluminium, beryllium, zinc, and copper. Also, SO$_4$ correlates negatively with pH (Fordyce and others 1995). These associations suggest strongly that arsenic and the associated trace metals are derived by oxidation of sulfide minerals. Concentrations of the trace metals diminish downstream of the mining area. Highest arsenic concentrations (up to 580 µg L^{-1}) 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 groundwaters (>15 m) are from an older carbonate aquifer. The shallow aquifer shows the greatest contamination with arsenic, with concentrations up to 5,100 µg L^{-1} (figure 10). In the shallow aquifer, 39% of samples collected randomly had arsenic concentrations >50 µg L^{-1}, while in the deeper aquifer, 15% exceeded 50 µg L^{-1} (table 11 see page 56) (Williams and others 1996).

The high-arsenic groundwaters of the Ron Phibun area clearly differ from many other high-arsenic groundwater provinces in Asia. In the shallow aquifer, conditions are more oxidizing than those prevalent in, for instance, the worst-affected areas of Bangladesh and West Bengal. The differences reflect the distinct geochemical reactions that are controlling the groundwater arsenic concentrations (section 3.3). In the groundwaters from the deeper aquifer of Ron Phibun conditions appear more similar to those from other high-arsenic aquifers in Asia and the

Figure 10. Simplified Geology of the Ron Phibun Area, Thailand, Showing the Distribution of Arsenic in Analyzed Groundwaters
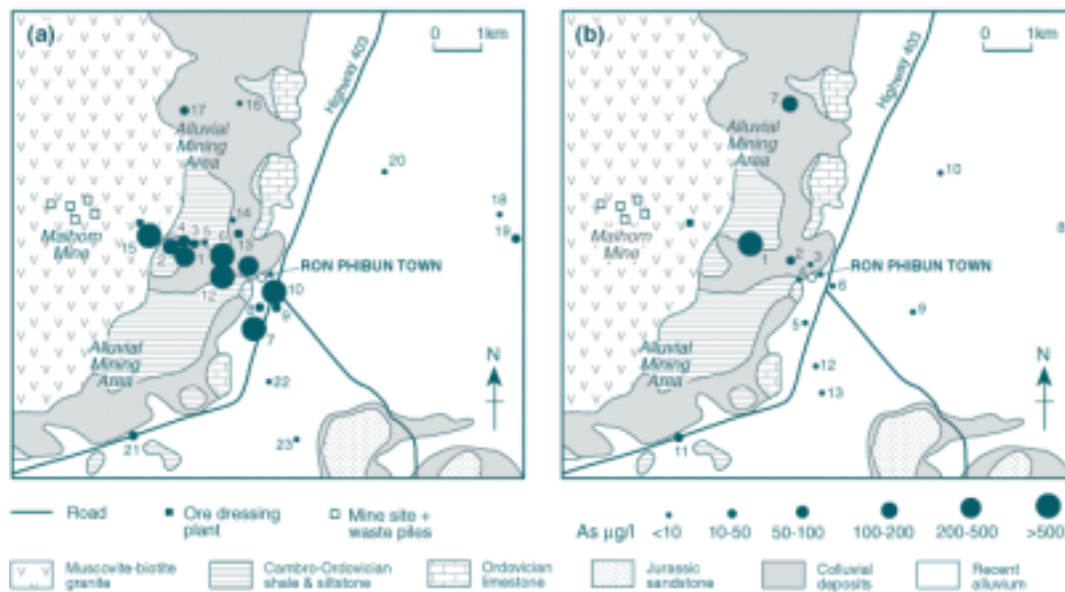
Note: The distributions are (a) arsenic in groundwater from shallow tubewells (<15 m depth); (b) arsenic in groundwater from deeper tubewells (>15 m). Numbers refer to samples given in Williams and others 1996.
Source: Williams and others 1996.

Table 11. Frequency Distribution of Arsenic Concentrations in Water from Phibun Area

Aquifer	Number of samples (%)			Total samples
	<10 µg L^{-1}	10–50 µg L^{-1}	>50 µg 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

Source: Williams and others 1996.

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 recognized 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 µg L^{-1} and 880 µg L^{-1} (Chakraborti and others 1999). Out of 146 samples analyzed, 8% were found to contain more than 50 µg L^{-1} arsenic (table 12). Three of these exceeding samples were from dug wells, one containing a concentration of 520 µg L^{-1}. Most were from tubewells, which were usually less than 50 m deep (range 10–75 m). Arsenic-related skin disorders have been recognized in a number of the villagers. Gold-mining activity has taken place in the local area, though the extent of mining and of mineralization is not documented. To date, no maps have been produced of Chowki block to indicate the distribution and scale of the problem.

Table 12. Frequency Distribution of Arsenic Concentrations in Groundwater from Chowki Block, Madhya Pradesh, India

Blocks	Number of samples (%)			Total samples
	<10 µg L^{-1}	10–50 µg L^{-1}	>50 µg L^{-1}	
Chowki	109 (75)	25 (17)	12 (8)	146

Source: Chakraborti and others 1999.

Other Areas

Although many areas of mining and mineralization 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 sulfide mineralized areas and hence the locations of such problems can be reasonably well predicted. Despite many mining-related problems, modern mining practices are designed to minimize environmental impacts. Environmental protection measures include criteria for siting and management of waste piles, control of effluents, and treatment of acid mine drainage.

3. 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 mobilization in water and the environment and the information that is available concerning spatial and temporal variability in the arsenic-affected aquifers of Asia.

The highest concentrations of arsenic tend to occur in sulfide 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 favored. Under most circumstances, the mobilization 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, sulfides, 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 ($Fe(S,As)_2$), which is probably the most important source of arsenic in ore zones. Other arsenic sulfides found in mineralized areas are realgar (AsS) and orpiment (As_2S_3).

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 sulfur, the other, more abundant, sulfide minerals also tend to have high concentrations of arsenic. The most abundant of these is pyrite (FeS_2). Concentrations of arsenic in pyrite, chalcopyrite, galena, and marcasite can be very variable but in some cases can exceed 10 weight percentage (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 in a number of aquifers. Pyrite is not stable in aerobic systems and oxidizes to iron oxides with the release of sulfate, acidity, arsenic, and other trace elements. The presence of pyrite as a minor constituent in sulfide-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.

Table 13. Typical Arsenic Concentrations in Rock-Forming Minerals

Mineral	Arsenic concentration range (mg kg⁻¹)
Sulfide minerals	
Pyrite	100–77,000
Pyrrhotite	5–100
Marcasite	20–126,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5,000
Oxide minerals	
Hematite	up to 160
Fe oxide (undifferentiated)	up to 2,000
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
Carbonate minerals	
Calcite	1–8
Dolomite	<3
Siderite	<3
Sulfate minerals	
Gypsum/anhydrite	<1–6
Barite	<1–12
Jarosite	34–1,000
Other minerals	
Apatite	<1–1,000
Halite	<3–30
Fluorite	<2

Source: Smedley and Kinniburgh 2002 and references therein.

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 percentage values (table 13), particularly where they form as the oxidation products of primary iron sulfides. Adsorption of arsenate to hydrous iron oxides is known to be particularly strong. Adsorption to hydrous aluminum and manganese oxides may also be important if these oxides are present in quantity (for example 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^{-1} or less. Carbonate minerals usually contain less than 10 mg kg^{-1} 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 sulfide 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.

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 chromated copper arsonate (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 localized. Most environmental arsenic problems recognized today are the result of mobilization under natural conditions.

Processes Involved in Mobilization

Oxidation of Sulfide Minerals

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

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

Table 14. Typical Arsenic Concentration Ranges in Rocks, Sediments, and Soils

Classification	Rock/sediment type	Arsenic range (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	1–2,900
	Evaporite deposits	0.1–10
	Coal	0.3–35,000
	Bituminous shale	100–900
Unconsolidated sediments and soils	Sediments	0.5–50
	Soils	0.1–55
	Soils near sulfide deposits	2–8,000

Source: Smedley and Kinniburgh 2002 and references therein.

The overall oxidation reaction leads to the generation of iron oxide (Fe(OH)$_3$) and dissolved sulfate (SO$_4$) as well as 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 sulfide 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 sulfide mineral oxidation have also been seen in mineralized 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 mineralized sedimentary aquifers of Wisconsin, United States. Here, historical abstraction of groundwater has led to aquifer dewatering and the accumulation of concentrations of arsenic up to 12,000 µg L^{-1} in the groundwater at the levels of

the mineralized veins (Schreiber, Simo, and Freiberg 2000). Oxidation of sulfide minerals has been advocated strongly by many workers in West Bengal (for example Das and others 1994) as the cause of groundwater arsenic problems in the Bengal basin. It is well known that authigenic sulfide 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 oxidize 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 oxidized (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 (for example phosphate) for adsorption sites may also be important. It is notable, for example, that reducing aquifers such as those of Bangladesh, West Bengal, and China have relatively high concentrations of dissolved phosphate. These are sometimes in excess of 1 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 (for example deltas). Burial of organic matter along with the sediments facilitates microbial activity, which plays an important role in the generation of the reducing conditions (BGS and DPHE 2001; McArthur and others 2001). The role of microbes in the reduction and mobilization process has been increasingly recognised in recent years (Oremland and others 2002; Islam and others 2004). The rates of the arsenic release reactions under such conditions are likely to be dependent on a number of factors, including rates of sedimentation, diffusion of gases, and microbial reactions, but they are likely to be relatively rapid on a geological timescale. The onset of reducing conditions and release from iron oxides is believed to be the main process controlling the high arsenic concentrations in the sedimentary aquifers of Asia.

The nature of the organic matter involved in the generation of reducing conditions in arsenic-affected aquifers has been disputed in recent years. Some have cited disseminated fine-grained solid and dissolved organic matter as the key redox driver (for example 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.

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 oxidizing to reducing conditions, usually just a few meters below the piezometric surface) (figure 11). Dug wells typically penetrate the shallowest levels of aquifers where conditions are relatively oxidized. Tubewells usually

Figure 11. Schematic Diagram of the Aquifers in Southern Bangladesh Showing the Distribution of Arsenic and the Configuration of Wells
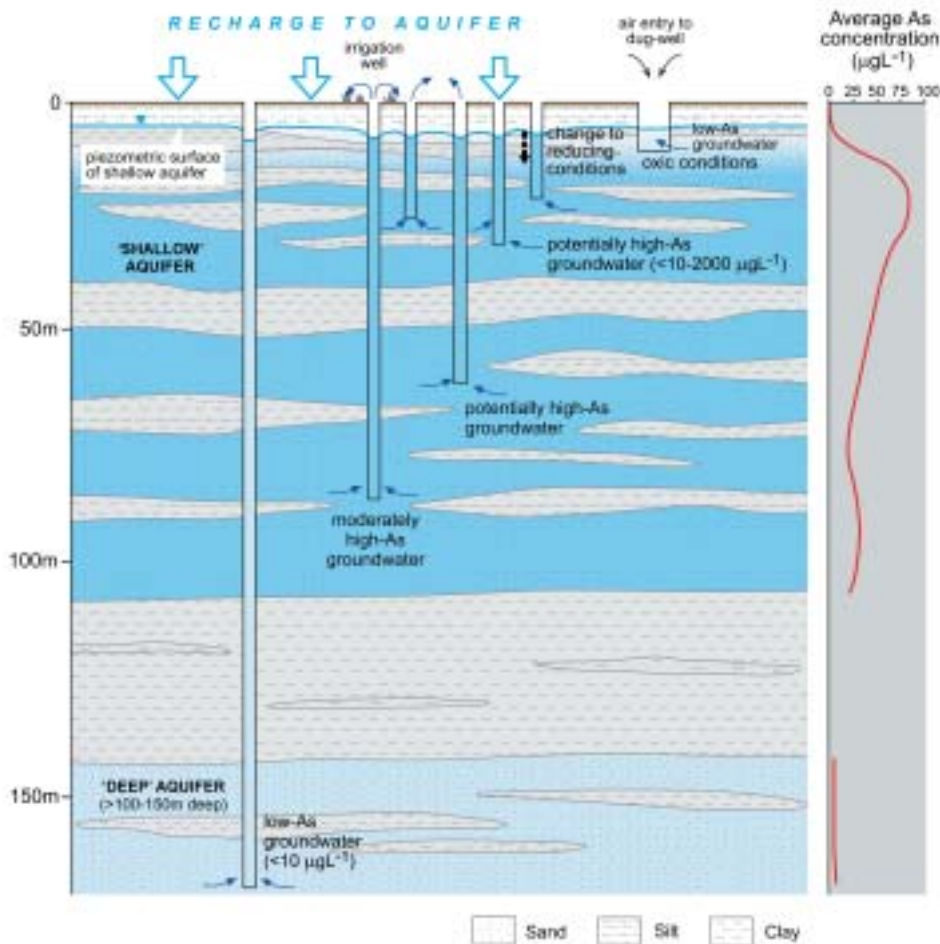
penetrate to deeper levels than dug wells in order to obtain better groundwater yields (although depths are usually the minimum required to achieve this). Entry of air to the open large-diameter wells also helps to maintain their relatively oxidized status in most circumstances (except in stagnant groundwater 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 oxidizing Quaternary sedimentary aquifers in, for example, the arid inland basins of Argentina (Smedley and others 2002) and southwest United States (Robertson 1989). Similar conditions have not been found to date in Asian sedimentary aquifers but the process may take place in some areas (for example 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, aluminum and manganese oxides can also adsorb arsenic and may be additional sources or 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 in 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 (for example 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 see page 66). It has been suggested that the deep aquifer 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 (BGS and DPHE

Figure 12. Sea Level Changes during the Last 140,000 Years
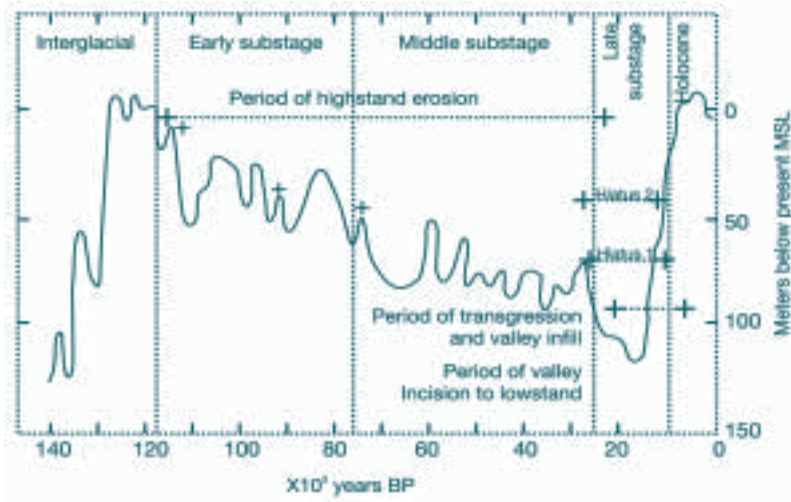
Source: After Pirazzoli 1996.

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 that may have a bearing on the groundwater arsenic concentrations. Certainly in Bangladesh, evidence suggests that the deeper Pleistocene sediments are dominantly more brown in color than the Holocene deposits and therefore appear to be more oxidized. More work on the sediment chemistry of the deep aquifers of the Bengal basin is required to investigate this further.

Impact of Human 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 human activities have contributed to the arsenic problems in different situations. It is clear that in sulfide mining areas such activities as excavating ore minerals, redistributing waste piles, and pumping mine effluent have exacerbated the problem. 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 natural 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

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 color 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 postglacial 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 probable 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 as the area is an internal drainage basin that 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.

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 human 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 subsurface redox conditions.

It is interesting 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 recognized high-arsenic groundwater provinces to allow them to be broadly categorized in terms of geology, hydrogeology, and the processes likely to be controlling arsenic mobilization. A number of risk factors for the development of high-arsenic groundwaters were identified and summarized 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 mineralization and mining activity (Ron Phibun, Thailand; Madhya Pradesh, India), and localized areas of geothermal activity, the documented cases included in chapter 2 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. Ancillary information such as low or no dissolved oxygen, low concentrations of sulfate, and high concentrations of dissolved organic carbon can also be of use in defining reducing aquifers (figure 13).

Figure 13. Classification of Groundwater Environments Susceptible to Arsenic Problems from Natural Sources

Environment Process Indicators

High-arsenic groundwater province

Geothermally influenced groundwater — **Low-temperature groundwater**

Nonmining areas — **Sulfide mining and mineralized areas**

Low rate of flushing:[a]
Young aquifer (Quaternary)
Low hydraulic gradient (deltas, closed basin)
Slow groundwater flow
Poor drainage
Arid/semiarid environment
Old groundwaters
High chemical spatial variability
Large volume of young sediments:
Large deltas and inland basin

Mixing/ dilution

Reducing:
Reductive desorption and dissolution
(Fe oxides) Confined aquifers

Oxidizing:
Desorption (Fe oxides)
Evaporation

Mineral dissolution
e.g. pyrite oxidation
Oxidizing or mildly reducing

Increased temperature
Increased salinity (Na, Cl)
High B, Li, F, SiO_2
High pH >7

Low Eh (<50 mV)
No dissolved oxygen
High Fe, Mn, NH_4
Low SO_4 (<5 mg L^{-1})
High alkalinity (>500 mg L^{-1})
Possibly high DOC (>10 mg L^{-1})

High pH (>8)
High alkalinity (>500 mg L^{-1})
Possibly high F, U, B, Se, Mo
Increased salinity
High Eh, DOC

High Fe, SO_4
Possibly low pH
Presence of other trace metals (Cu, Ni, Pb, Zn, Al, Co, Cd)

E.g. Bangladesh; China (Inner Mongolia); Taiwan; West Bengal in India; Nepal
Possibly: Cambodia; some parts of northern China; Lao PDR; Vietnam

E.g. Pakistan
Possibly: Some parts of northern China

Note: Not all indicators of low flushing rates necessarily apply to all environments.
Source: Smedley and Kinniburgh 2002.

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 oxidizing conditions in some arid and semiarid inland (closed) basins. As noted above, these groundwaters are typically characterized 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 oxidizing, high-pH groundwater provinces recognized 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 areas 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 (for example 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 oxidizing, 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 recognized 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 centimeters. 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 homogenization 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 µg L^{-1} and 50 µg 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 flood plains. The occurrence of local arsenic hotspots observed in, for instance, Bangladesh aquifers may be explained by the localized occurrence of fine-grained sediments in inside meanders and oxbow 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 handpumped 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 meters) 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 premonsoon, syn-monsoon and postmonsoon 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 postmonsoon 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
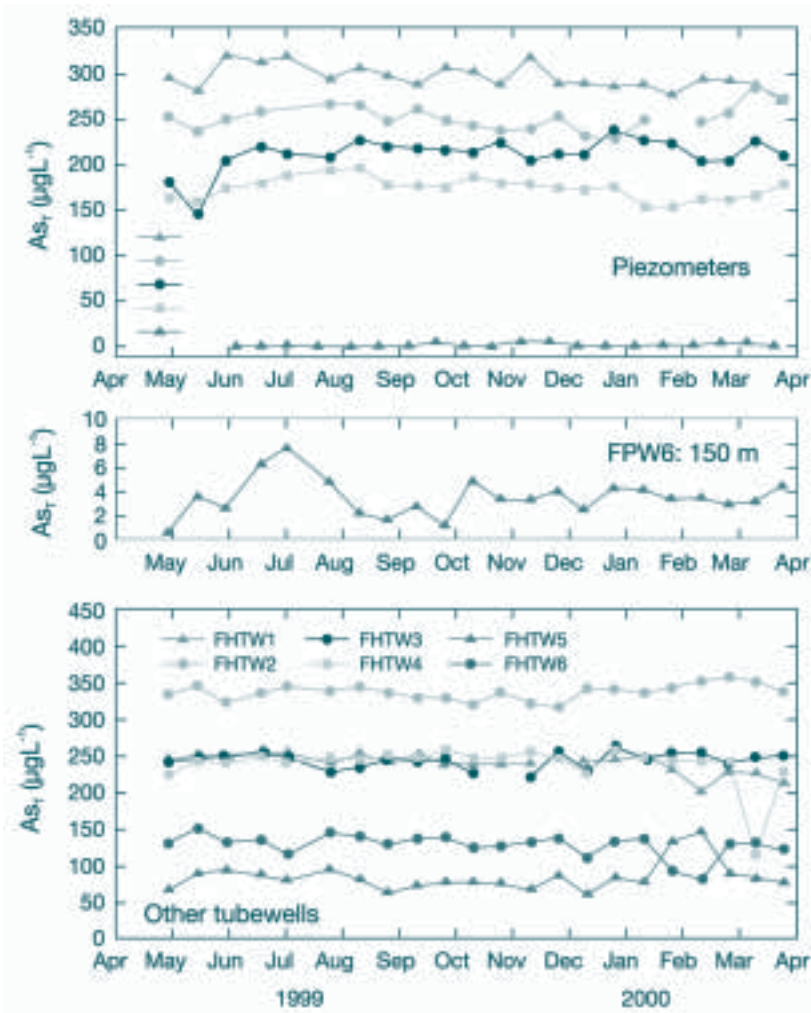
Source: BGS and DPHE 2001.

were once arsenic free have become contaminated with time (for example 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 conditions. They may also vary if particulate contents vary with time and water samples taken from them are not filtered. Despite these possibilities, groundwater in three dug wells from northwest 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 μg L^{-1}, with only two individual measurements from the wells exceeding 10 μg 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 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.

4. 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 realization that the mode of occurrence of arsenic in water can vary substantially. The mechanisms of arsenic occurrence in water in mining and mineralized 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. The options, risks, and potential mitigation strategies are summarized in table 15, at the end of this chapter.

Mining and Mineralized Areas

In areas with rich deposits of sulfide minerals, both surface waters and groundwaters are potentially vulnerable to high arsenic concentrations. Other toxic trace elements may also be present in excessive concentrations (for example 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 localized, on the scale of a few kilometers around the site of mineralization. Mitigation of the problem therefore centers 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 arsenic-affected 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 recognized arsenic problems, the majority are composed of young sediments at shallow depths of 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, the scale 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 prioritization 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 (for example 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 programs in such susceptible aquifers are needed regardless of local geological variations.

The distributions of arsenic in different districts of Bangladesh vary widely (BGS and PDHE 2001). The worst-affected districts identified from the BGS and DPHE (2001) study were (percentage of samples with arsenic concentrations greater than 50 µg L^{-1} 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 favor 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 µg L^{-1} and 46% exceeded 10 µg L^{-1}. This means that 73% and 54% of wells had concentrations below these limits respectively. Also, 24% of samples analyzed had concentrations below the analytical detection limit, usually 0.25 µg L^{-1} or 0.5 µg L^{-1}. The districts of Thakurgaon, Barguna, Jaipurhat, Lalmonirhat, Natore, Nilphamari, Panchagarh, and Patuakhali all had no samples with arsenic >50 µg L^{-1} 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 example, for washing and other domestic purposes, provided the wells are labeled 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 (for example high manganese, uranium, boron concentrations) or can cause problems with acceptability (high salinity, iron, ammonium concentrations). In arid areas (for example 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 of good quality in respect of arsenic concentrations may not necessarily be of 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, Chen, and Greene 1994) indicates that many dug wells contain water complying with the WHO guideline value of 10 μg L^{-1} and most comply with the national standard of 50 μg L^{-1}.

Despite this tendency, a rather different situation is apparent for groundwater from dug wells in Inner Mongolia. As shown in earlier section, dug wells in the Huhhot basin were found to contain groundwater with arsenic concentrations up to 560 μg L^{-1} 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 program to confirm the concentration ranges. Care should also be taken in analyzing 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 handpumps 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 μg L^{-1}). 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 μg L^{-1}. 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, Ahmed, and others (2003) 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, Ahmed, and others (2003) 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 meters 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 (a) their lateral extent; (b) their depth ranges (as demonstrated by the van Geen, Ahmed, and others 2003 example); and (c) 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 modeling 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. Modeling 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 contains arsenic concentrations in the range $<1–308$ µg 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 (for example galvanized iron, tiled surfaces) but that 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 µg 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 localized to within a few kilometers of the mining activity (Smedley and Kinniburgh 2002), although those affected by geothermal inputs can be more widespread.

Surface waters in 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 µg 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 µg L^{-1} (in March 1999) although repeat sampling (in December 1999) gave a value of 2.7 µg 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, for example, the initial concentration and the river baseflow index (proportion of groundwater present).

A worse problem associated with the use of surface water is the potential risk from bacterial and other waterborne 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.

Table 15. Risks Associated with the Use of Drinking Water from Various Sources at Various Scales and Potential Mitigation Strategies

Source	Risk for supply	Mitigation strategy		
		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 concentrations of other inorganic constituents (e.g. Mn, U, NH_4, 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	n.a.	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	n.a.
	Bacterial and other waterborne diseases, high particulate loads	Disinfection, filtration	Well protection: sanitary seals, handpump installation, water disinfection, periodic cleaning. Relocate wells away from pollution sources	n.a.
	Other inorganic water quality problems (e.g. nitrate, uranium, manganese)	Difficult	Water treatment difficult. Relocate wells away from pollution sources (nitrate)	n.a.
	Arsenic may exceed prescribed limits	Water testing necessary. Treatment difficult	Water testing necessary. Treatment difficult	n.a.
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	n.a.	n.a.
	Bacterial contamination	Storage protection, disinfection	n.a.	n.a.

n.a. Not applicable.

5. 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 mineralization 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. First, the scale of the problem needs to be assessed. Second, where problems exist, it is necessary to find out whether or not the situation is becoming worse with time. Third, 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 program 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 randomized 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 program requires consideration of the analytical capability of the local laboratories. In some cases, development of laboratory capability (for example quality assurance procedures, training, equipment upgrades, increased throughput) may be required and should be built into the testing program.

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 by which such standards such as 50 µg L^{-1} or 10 µg L^{-1} are exceeded). 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 earlier section that our ability to define with accuracy where low-arsenic aquifers are likely to be 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 mineralization or geothermal inputs. However, given the potential health risks associated with arsenic in drinking water, there is an argument for some randomized 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 (for example 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 µg L^{-1}) should trigger a program 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 (such as 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 (for example 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 (table 16 see page 82). 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 organizations may be required. The size of the prior investigation work should be commensurate with the size of the intended water supply program, amounting to say 5-10% of the projected implementation cost.

Table 16. Arsenic Testing Strategies in Potential High-Arsenic Groundwater Provinces

Area	Existing drinking water wells	New drinking water wells
Untested areas	Randomized 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.

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 randomized 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^2. 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 localized 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 seen to be the southeastern part of Bangladesh. Subsequent surveys by various organizations may have refined the data distributions, but 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 µg L^{-1}. This figure compares well with an earlier estimate of exceedances above 50 µg L^{-1} for the whole country (26%) based on data from BGS, DPHE, and other organizations (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 (for example the deep (Pleistocene) aquifer in Bangladesh) should also be tested on a randomized basis to assess their potential as alternatives. The data need to be analyzed 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 recognized, 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. 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 (for example 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 μg L^{-1}, the sensitivity of newer designs is better. Wherever possible, capability to test reliably at 10 μg L^{-1} should be aimed for. Wherever possible, a subset of samples analyzed 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 program (box 1 see page 31).

Past hydrogeochemical investigations of high-arsenic aquifers have shown correlations with other elements (for example iron, manganese) but these are rarely sufficiently significant to be useful in a practical sense. 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 modeling 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 color 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-colored sediments at depth are most likely to contain groundwater with low concentrations of arsenic and iron. Color 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 recognized 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 see page 31). Analytical problems should therefore be expected and variations viewed with skepticism 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 neighboring aquifers.

Shallow Sedimentary Aquifers with Recognized Arsenic Problems

On the scale of arsenic problems recognized 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 for water from dug wells (especially those with concentrations >50 µg L^{-1}, which should be retested to verify the concentration) and for treated water that has 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 µg 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 periods of hours. Observation of seasonal changes requires weekly or fortnightly monitoring. Longer-term changes require monitoring 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 (five 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 handpumped 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 programs need to be undertaken in specific areas to obtain further monitoring data. On a research scale, this is a relatively easy program 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 that persist.

Ideally, a program 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 recognized high-arsenic aquifers is also required. Such programs 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 programs 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 μm 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 involves acidification, and at any given time the result will include suspended as well as dissolved arsenic.

6. Concluding Remarks

High arsenic concentrations recognized 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 Assam, Arunachal Pradesh, Bihar, Manipur, Meghalaya, Nagaland, Uttar Pradesh 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. High-arsenic 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 yields or high groundwater salinity. Other Quaternary sedimentary aquifers in Asia have not been investigated and so their arsenic status is unknown. Some localized groundwater arsenic problems relate to ore mineralization and mining activity (for example 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 mobilization in groundwater, as well its derivation from different mineral sources. The most important mineral sources in aquifers are metal oxides (especially iron oxides) and sulfide 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 oxidizing (aerobic) conditions. These tend to occur in arid and semiarid 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 United States, 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.

Mobilization of arsenic in mineralized and mining areas is linked to the oxidation of sulfide minerals. Here, occurrences can affect both surface waters and groundwaters but the affected areas are typically localized (a few kilometers around the mineralized 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 regarding the nature of the source, mobilization, 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 meters. 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 in the short term (daily), the medium term (seasonally), and 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 (for example Quaternary sediments in Cambodia, Myanmar, Nepal). However, the toxicity of arsenic is such that it should also be 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. Randomized 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 (for example 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 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 sulfide (FeS_2), 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 about 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.

Mineralization. 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 sulfide; reducing conditions commonly occur in confined aquifers.

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